



Great Smoky Mountains National Park 2013 Water Quality Annual Report

Natural Resource Data Series NPS/GRSM/NRDS—2014/701



Lost Bottom Creek

ON THE COVER

Lost Bottom Creek at Palmer Creek trail crossing

Photograph by: Mary Ann Grell, University of Tennessee, Knoxville, November 2006.

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Contents

	Page
Figures.....	v
Tables	vi
Appendices.....	vii
Executive Summary	viii
Acknowledgments.....	viii
List of Terms, Small Glossary, Acronyms, or Contacts	ix
1.0 Introduction.....	1
2.0 Noland Divide Watershed.....	1
2.1 Introduction.....	1
2.2 Study Activities and Methods.....	2
2.3 Annual Precipitation Volume	4
2.3.1 Seasonal Precipitation Patterns	5
2.3.2 Precipitation pH Profile	6
2.4 Annual Deposition Rates for Chemical Constituents	7
2.4.1 Sulfate Deposition Profile.....	7
2.4.2 Nitrogen Deposition Profile.....	8
2.4.3 Nitrogen Speciation Shift.....	8
2.5 Soil Water Chemistry	9
2.6 Stream Water Chemistry.....	10
2.7 Atmospheric Source / Deposition Correlations	11
3.0 Park-wide Stream Survey	14
3.1 Park-Wide Water Chemistry: Watershed Summary.....	14
3.3.1 Abrams Creek Water Chemistry	16
3.3.2 Cataloochee Creek Water Chemistry.....	17
3.3.3 Cosby Creek Water Chemistry	17
3.3.4 Little River Water Chemistry.....	19
3.3.5 Oconaluftee River Water Chemistry.....	20

Contents (continued)

	Page
3.3.6 West Prong of the Little Pigeon River Water Chemistry	20
3.3.7 Hazel Creek Water Chemistry	22
3.4 Park-Wide Water Chemistry: Temporal Trends	24
3.5 Park-Wide Water Chemistry: Toxicological Thresholds	24
3.5.1 pH.....	24
3.5.2 Aluminum	25
3.5.3 Zinc	25
4.0 Laboratory Data Quality Evaluations	26
4.1 Ion Chromatography Data Quality	26
4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry Data Quality	27
4.2.1 Detection Limits, Field Blanks, and Laboratory (Instrument) Blanks.....	28
4.2.2 Quality Control Check (QCC) Solutions	29
4.2.3 Analytical Precision: Matrix Duplicate Analysis	29
4.2.4 Analytical Accuracy: Matrix Spike Analysis	30
4.3 USGS QA Reference Samples (Inter-Laboratory Comparison Study)	30
4.3.1 IC Results.....	31
4.3.2 ICP Results.....	32
4.4 Ion Charge Balance Check	32
4.5 General Data Quality Assurance Improvements	34
Literature Cited	35

Figures

	Page
Figure 1. Map of Noland Divide watershed showing water quality monitoring stations (OS = open site, TF = throughfall site, SW and NE = streamlet sites).....	2
Figure 2. Total annual precipitation volumes (in centimeters) at throughfall (TF) and open site (OS) in the NDW	5
Figure 3. Distribution of monthly precipitation totals, averaged over all years (1991 to present).....	5
Figure 4. Annual mean pH of precipitation collected at TF (solid circles) and OS (open circles), shown with standard error bars	6
Figure 5. Total sulfate (in equivalents per hectare per year; eq/ha/yr) entering NDW via precipitation measured at TF and OS.....	7
Figure 6. Total inorganic nitrogen (nitrate + ammonium; eq/ha/yr) entering NDW via precipitation measured at TF and OS.....	8
Figure 7. Annual mean percentage of ammonium in T.I.N. in TF precipitation, and the corresponding annual mean pH.....	9
Figure 8. Correlation between mass of sulfur (tons x 1000) emitted from regional fossil fuel power plants and the annual total equivalents of sulfur per hectare deposited at the TF site	12
Figure 9. Correlation between mass of nitrogen (tons x 1000) emitted from regional fossil fuel power plants and the annual total equivalents of nitrogen (NO ₃ + NH ₄) per hectare deposited at the TF site.....	13
Figure 10. Currently sampled sites for the GRSM Park-wide stream survey water quality monitoring program	14

Tables

	Page
Table 1. Summary data statistics for conductivity, pH, common anions and base cations in soil lysimeter samples collected in 2013 and in all prior years.	10
Table 2. Summary data statistics for conductivity, pH, common anions and base cations in streamlet water samples (NE and SW) collected in 2013 and in all prior years.	11
Table 3. Selected water chemistry for 2013 and all prior years, organized by drainage basins (standard error of the mean in parentheses)	15
Table 4. Summary of water chemistry data for Abrams Creek sampling sites	16
Table 5. Summary of water chemistry data for Cataloochee Creek sampling sites	18
Table 6. Summary of water chemistry data for Cosby Creek sampling sites	19
Table 7. Summary of water chemistry data for Little River sampling sites.....	19
Table 8. Summary of water chemistry data for Oconaluftee River sampling sites.....	20
Table 9. Summary of water chemistry data for West Prong of Little Pigeon River sampling sites.....	21
Table 10. Summary of water chemistry data for Hazel Creek sampling sites	23
Table 11. Ion chromatograph instrument and method QA summary (anions and cations)	27
Table 12. ICP-AES detection limits and sample blank results.	28
Table 13. ICP-AES accuracy (based on prepared QCC standards)	29
Table 14. ICP-AES method precision and bias (duplicate split samples and spiked samples)	30
Table 15. Ion chromatograph blind-sample accuracy QA summary (anions and cations)	31
Table 16. ICP-AES blind-sample accuracy for USGS certified reference samples (percent)	32
Table 17. Ion charge balance calculations for Noland Divide Watershed samples (streamlet, precipitation, and soil water).....	33

Appendices

	Page
Appendix A: Algorithm for calculating monthly and annual precipitation volumes and deposition mass for NDW samples	36
Appendix B: Methods for Chemistry Analysis Performed at the University of Tennessee –Knoxville.....	39
Appendix C: Site Locations for the Park-wide Stream Water Quality Program.	40
Appendix D: General Data Quality Assurance Improvements.....	42

Executive Summary

The Great Smoky Mountains (GRSM) National Park annual Water Quality (WQ) Monitoring Program consists of: 1) detailed hydrologic and WQ monitoring at Noland Divide, a high-elevation forested site, and 2) Park-wide stream survey monitoring. This report gives a summary of all data collected for the GRSM monitoring program, from 1991 through the current year 2013. The annual mean pH of precipitation samples collected at the Noland Divide site was 5.34 for throughfall (TF) and 5.27 for Open Site (OS) wet deposition only. Precipitation pH at these two sites have been trending upward since 2007; prior to that year TF pH remained below 4.4 and OS pH below 4.0. Annual sulfate deposition loads at Noland Divide in post-2008 years (< 700 eq/ha/yr) have been consistently less than in pre-2008 years (>1,100 eq/ha/yr). In 2013, TF sulfate deposition was 695 eq/ha/yr. Evidence indicates that reduction in sulfate deposition likely has resulted from emission reductions at two coal-fired power plants within 100 miles of the GRSM. The 2013 TF data represented a continuation of a generally decreasing trend since 2008 in deposited total inorganic nitrogen (T.I.N.) below 900 eq/ha/yr. In 2013 T.I.N. for TF was measured at 344 eq/ha/yr. In general during this period since 2008, ammonium represented a greater portion of T.I.N, which is converted by soil microbes to nitrate through mineralization and nitrification resulting in increased acidity. However, soil pH in the upper horizon for 2013 was observed to generally be higher than long-term measurements. Soil water chemistry data is highly variable over time and needs additional analysis. Overall in 2013, sulfate, nitrate, and base cations were lower in soil water concentrations than historic measurements. Streams at Noland Divide had an average pH of 5.81 and 6.01 for the NE and SW streamlets, respectively, and remain in an acidified condition with acid neutralizing capacity (ANC) averaging 11.4 and 20.3 $\mu\text{eq/L}$ for the NE and SW streamlets, respectively. Among the Park-wide stream survey sites, 21 of the 197 samples collected during 2013 had a pH of less than 6.0, and eleven samples had a pH less than 5.5 (a toxic threshold impairing trout growth). Seven samples had dissolved aluminum concentrations greater than or equal to 0.2 mg/L, a known toxic threshold for that metal. The locations where these exceedences occur appear to be associated with aluminosilicate mineral weathering from soils, resulting in leaching of dissolved metals into adjacent streams. In 2013, the mean pH was > 6.0 in all monitored streams Park-wide; however, each watershed has unique factors (i.e., bedrock geology, soil, and vegetation) that greatly influence biogeochemistry processes, thus the fate of acid pollutants entering the GRSM and transport to the streams. Park-wide data from both monitoring programs provide critical information to assess aquatic resource health. It also supports BGC-Pn-ET model calibration and verification for estimating critical acid deposition loads, and predicting possible recovery trends.

Acknowledgments

Monitoring was accomplished under a cooperative agreement between the U.S. National Park Service, Southeast Region and the University of Tennessee (Knoxville) under the Southern Appalachian Cooperative Ecosystem Studies Unit, CESU Host Cooperative Agreement No. H5000095040, Task Agreement Order No. J5471090012. The University of Tennessee identifies task agreement as Research Account No. R01-1334-292. We thank the volunteer support of Trout Unlimited for the bimonthly water sample collections. University of Tennessee students volunteer time to support research activities. We thank Meijun Cai, a former doctorate student who continues to be a valuable resource for explanations to previous data analyses.

List of Terms, Small Glossary, Acronyms, or Contacts

ANC	Acid Neutralizing Capacity
BDL	Below Instrument Detection Limit
CEE	Department of Civil and Environmental Engineering
CV	Coefficient of Variation
DI	Deionized Water
eq/ha/yr	Equivalents per hectare per year
GRSM	Great Smoky Mountain National Park
IC	ion chromatograph or ion chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
N	Nitrogen
NADP	National Atmospheric Deposition Program
NDW	Noland Divide Watershed
NPSTORET	National Park Storage and Retrieval
OS	Open Site (<i>Noland Divide Study Site</i>)
QA/QC	Quality Assurance / Quality Control
QCC	Quality Control Check
T.I.N.	Total Inorganic Nitrogen
TF	Throughfall (<i>Noland Divide Study Site</i>)
UTK	University of Tennessee - Knoxville
WQ	Water Quality

1.0 Introduction

Since the 1980's, national air quality monitoring has shown that the Great Smoky Mountain National Park (GRSM) receives elevated levels of acid pollutants from atmospheric deposition sufficient to cause stream acidification (Shubzda et al. 1995; NADP 2009; Sullivan et al. 2007; Silsbee and Larson 1982; Cai et al. 2011a, 2012). Acid pollutants originate from emissions of combustion by-products from sources such as regional coal-fired power plants, in addition to vehicular exhaust (Chestnut and Mills 2005; Stachurski and Zimka 2002; Stoddard 1994; Weathers et al. 2006). Commonly observed in the eastern United States, high elevation watersheds with naturally base-poor cation buffering capacity tend to be most vulnerable to the effects of acid deposition (Hyer et al. 1995; Driscoll et al. 2001). Most streams in the GRSM are low in acid neutralizing capacity (ANC), and very susceptible to chronic and episodic acidification (Robinson et al. 2008; Deyton et al. 2008; Neff et al. 2013). Low-ANC streams affected by acidification can transport high concentrations of aluminum and other acid-cations, released from soil minerals (through altered weathering). Such conditions adversely affect aquatic organisms in those streams. When soil water pH drops below 5, soluble monomeric aluminum (Al_{IM}) can be released entering nearby streams, and Al_{IM} can be toxic to aquatic biota (Baldigo and Murdoch 1997; Neff et al. 2009). Based on initial studies in the 1980s linking stream water quality and atmospheric acid deposition, the GRSM initiated a long-term continuous water quality (WQ) monitoring program in the early 1990s to investigate and monitor conditions within the GRSM. The current GRSM WQ program includes: 1) detailed hydrologic and WQ monitoring at Noland Divide (a high-elevation forested watershed); and 2) the Park-wide stream survey designed to characterize water quality under base-flow conditions. In this report, data are summarized for 2013, and compared with prior years' data to identify long-term trends in WQ parameters.

2.0 Noland Divide Watershed

Noland Divide watershed (NDW) was selected as a part of the long-term water quality-monitoring program in 1991 after completion of the Integrated Forest Study. The Integrated Forest Study was an American and European program to study acid rain effects on forest nutrient cycling, in which the NDW was one of several sites studied (Johnson and Lindberg 1992; Lindberg and Lovett 1992). Ongoing monitoring at NDW continues to assess effects of stream acidification by better understanding the biogeochemical processes as deposited acid pollutants are transported by water from forest cover into the soils and then to streams. In addition, NDW data are used in the calibration of the BGC Pn-ET Model which will predict future conditions for various acid deposition scenarios and estimate critical loads for the GRSM (Zhou et al. 2011).

2.1 Introduction

NDW is located in the GRSM about a half-mile from Clingman's Dome, on the border of North Carolina and Tennessee at 35° 34' N latitude and 83° 29' W longitude. NDW is a small, 17.4 ha forested watershed ranging in elevation from 1,680 m to 1,920 m (Figure 1). Two adjacent first-order streams originate from this watershed (NE and SW streamlets) and merge to form Noland Creek. The mean annual air temperature measured at a climate station, located about 100 m below the watershed outlet, is approximately 8.5°C, ranging from -2°C in January to +18°C in

July, with a frost-free period from May through September (Shanks 1954; Van Miegroet et al. 2001). The annual precipitation ranges from 200 cm to 300 cm, 10% of which is accounted by snow (Johnson et al. 1991; Johnson and Lindberg 1992). In the 1990s, NDW's vegetative overstory consists of old-growth red spruce, and interspersed patches of dead Fraser fir (Nodvin et al. 1995).

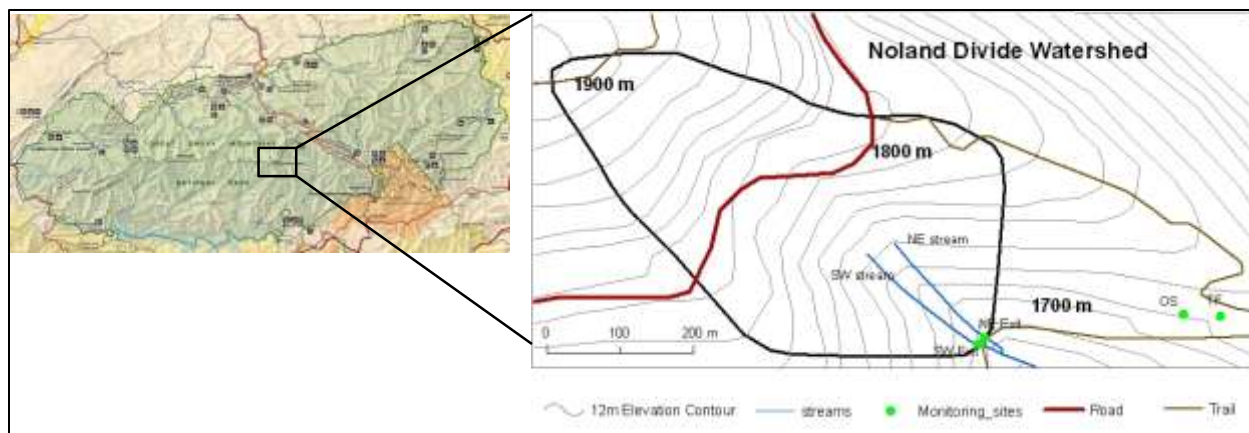


Figure 1. Map of Noland Divide watershed showing water quality monitoring stations (OS = open site, TF = throughfall site, SW and NE = streamlet sites).

Soils in the NDW are inceptisols with spodic characteristic, classified as Dystrochrepts or Haplumbrepts (McCracken et al. 1962; Van Miegroet et al. 1993). They have a silt loam to sandy loam texture, and are generally shallow throughout the NDW. Johnson and Lindberg (1992) characterized the NDW soil as consisting of a 4 cm thick Oi + Oe horizon of needles and leaves, a 4-cm thick Oa horizon of organic humus, an 8 cm thick A horizon of dark, reddish-brown, mucky loam, a 27-cm thick Bw horizon of dark brown, sandy loam, a 35 cm thick Cb horizon of dark, yellowish-brown loam, a 20+ cm thick C horizon of olive-brown, loamy sand, and underlying sandstone bedrock. Underneath the soil is massive thick-bedded and low porosity Thunderhead sandstone, composed of quartz and potassic feldspar (King et al. 1968).

2.2 Study Activities and Methods

Five NDW hydrological stations were installed to monitor the potential effects of long-term acid deposition (Figure 1). These stations include: wet precipitation (open site, OS), throughfall (TF), soil water from lysimeters, and two streamlets (southeast, SE; and northeast, NE sites). This monitoring design provides a means to assess impacts from acidic deposition, both wet and dry deposition (OS, TF sites), effects of soil biogeochemical processes on pollutant fate and transport, and stream acidification response based on levels of atmospheric acid inputs to the watershed.

OS and TF samples are collected every two weeks except during extreme winter weather. Wet-only precipitation is collected at the OS site free of tree cover/canopy. During 2013, the atmospheric deposition sampler consisted of the original equipment installed in 1991. The past two years age influenced equipment performance requiring replacement several times of motor gears which operate cover control arms. On December 12, 2013, the original deposition sampler was replaced with a new ADS00-120 Sampler (N-CON Systems, Inc., Georgia). This new unit required more power therefore additional batteries and solar panels were installed in June 2014.

TF is collected at an “under tree canopy” site, located at the same elevation. During winter operations starting in December, two TF collection sites are situated approximately 50 m apart within an electric fenced area to protect plastic sample buckets from bear damage. During summer operations, nine buckets are used dispersed in the same general fenced area. OS rain and TF water are collected in new plastic bags inside 5-gal plastic buckets, and weighed prior to being subsampled into clean plastic bottles. Precipitation volumes collected since the previous collection date are estimated based on the measured field weight and the area of the bucket opening, and converted to centimeters per hectare (cm/ha). More details on TF computations follow.

Procedures for computing annual and monthly deposition load estimates at OS and TF sites were reviewed, and documented algorithms for those computations are in Appendix A. Different approaches to loading computations can lead to inconsistencies. Inconsistencies can result from how one weights sample concentrations per water volumes collected between sample periods. Sample collections occur roughly bi-weekly, but field conditions can force slight adjustments to the target schedule, so a given sample does not represent a consistent interval of days between collections. This can affect how load estimates (product of concentration and volume per unit of time) are weighted. For instance, a procedure where sample concentrations are averaged over an annual collection set and then applied to a total annual water volume will lead to less accurate load estimates. Because the OS and TF precipitation amounts are not measured, and precipitation chemistry not analyzed, on a daily basis, how a precipitation sample’s “point concentration” is applied to the precipitation sample’s volume and distributed over the multiple-day collection period must be determined to get a load (mass per unit of time). What assumptions are used to infer intra-period distribution of precipitation can have a significant effect on monthly precipitation estimates causing inconsistencies in evaluating monthly air-borne pollutant mass deposition. Monthly estimates for loads will be more vulnerable to these inconsistencies than annual estimates because the larger number of samples tends to reduce statistical errors associated with individual monthly estimates.

A large source of variance is in precipitation samples representing collection periods that span sequential months (mostly winter months). On average, a precipitation sample retrieved at the beginning of a month (e.g., within the first week of the month) can contain some proportion of water that fell in the previous month (depending on when the prior sample was retrieved). To date, samples spanning sequential months generally have been assigned entirely to the month in which the sample was retrieved. Doing so, however, causes the precipitation amount (and associated air-pollutant deposition mass) to be biased high in the current month and biased low in the previous month, on average. Depending on when samples are retrieved, and the duration of the interval collection period, this error can propagate to substantial proportions.

Coordinating UT precipitation monitoring data with independent precipitation data from sources such as the National Weather Bureau or the National Park Service at GRSM is a labor-intensive method of determining a realistic distribution pattern between sample collection dates. A more practical, and defensible, method of allocating the amount of precipitation in a given sample among adjoining months is to proportion measured precipitation volumes by day. This calculation approach, outlined in Appendix A, is used by the University of Tennessee –

Knoxville (UTK), Department of Civil and Environmental Engineering (CEE) in this and all future reports.

Stream water quality and discharge are measured at the watershed outlet of NDW, in two adjacent “streamlets,” the southwest (SW) and northeast (NE) streams. At each streamlet, flows are obtained from continuous data collected with 3-ft H-flume and GlobalWater® WL16 stage recorders. Stage recorders measure flow depth every 15 minutes, and discharge is computed from measured water depth through the standard USDA H-flume formulas. General water quality parameters (pH, conductivity and temperature) are continuously monitored with Eureka Manta II sondes (purchased new in August 2012). Sonde data collection in the SW started in July 1991 and the NE sonde data began in April 1998. Data sondes record data every 15 minutes. Grab samples of stream water are collected from the NE and SW streams every two weeks for chemical analyses.

Soil water samples from three distinct soil horizons (A, Bw, and Cb) are collected by 12 ceramic suction lysimeters in quadruplicate (four per soil horizon) in which a vacuum is generated by a hydraulic gravity-drop system. Soil lysimeters are located adjacent to the TF site within the electric fenced area (Figure 1). Soil water is collected on a biweekly or monthly basis dependent on the amount of rainfall and volume in the collection bottles (100 ml minimum). Maintenance in December 2013 entailed replacing the old ceramic lysimeters and modifying the vacuum system. Twelve new suction lysimeters were installed with four units per A, Bw, and Cb horizons, approximating the previous lysimeter locations. The new suction lysimeters are Model SW-074 manufactured by SMS, Inc. consisting of 0.875 in dia. (OD) porous stainless steel (SS) construction, total length equal to 4.5 inch and porous SS length equal to 3.7 inch. A small vacuum pump powered by two 12-V batteries generates a negative pressure connected to a manifold apparatus where vinyl tubing connects to individual collection bottles and lysimeters.

All water samples from OS, TF, SW and NE streams, and lysimeter soil water sites are transported from the GRSM to the UTK-CEE WQ laboratory for chemistry analyses. Parameters and corresponding analytical methods are listed in Appendix B. Data quality was evaluated and documented through a program of QA checks for all analyses (Section 4.0). The NDW grab sample dataset for 2013 consists of 110 samples: 14 samples from OS, 19 samples from TF, 18 samples each from the NE and SW streamlets, and 41 from the three soil lysimeter horizons. Samples collected on 19 September 2013 were analyzed only for metals because they were inadvertently acidified prior to analysis. The following sections summarize the 2013 data, and the comparison between them and historical NDW data collected between 1991 and 2012.

2.3 Annual Precipitation Volume

The annual rainfall volumes collected during 2013 were 223 cm at the TF and 139 cm at the OS (Figure 2). Annual cumulative precipitation volumes in all prior years (excluding the partial first year of data collection, 1991) ranged between 135 and 277 cm at TF and between 91 and 275 cm at OS. Although 2013 appears to have been a typical precipitation year for the NDW, adjustments have been made to field equipment to improve the accuracy of the precipitation collection process. Also note that data for precipitation at OS were not collected between January and May in 2001; precipitation is underestimated for that year.

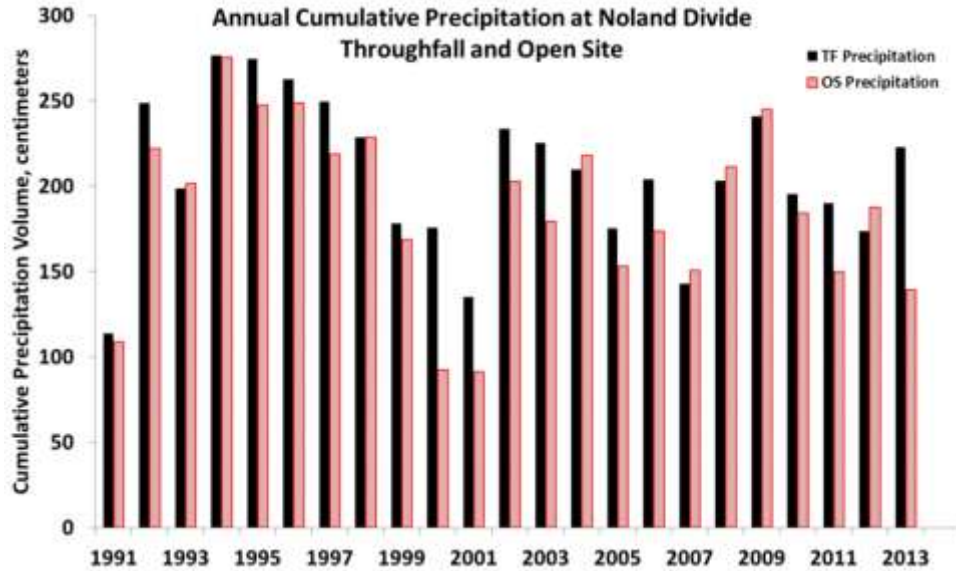


Figure 2. Total annual precipitation volumes (in centimeters) at throughfall (TF) and open site (OS) in the NDW. Sampling in 1991 began mid-year; that year's data do not represent the entire year.

2.3.1 Seasonal Precipitation Patterns

Seasonal precipitation patterns are relevant to acid-pollutant deposition in the Park; higher amounts of precipitation result in higher wet-deposition mass-loading of pollutants. Monthly precipitation totals were averaged over all years of record (since 1991) (Figure 3). The error-bars represent the 95% confidence interval of the mean. A clear seasonal pattern is evident, with nearly twice as much precipitation falling in winter months (January) than in summer months (July). The effect of canopy interception and evaporation in NDW is seen by the lower amounts of precipitation reaching the understory in summer months (OS volume minus TF volume).

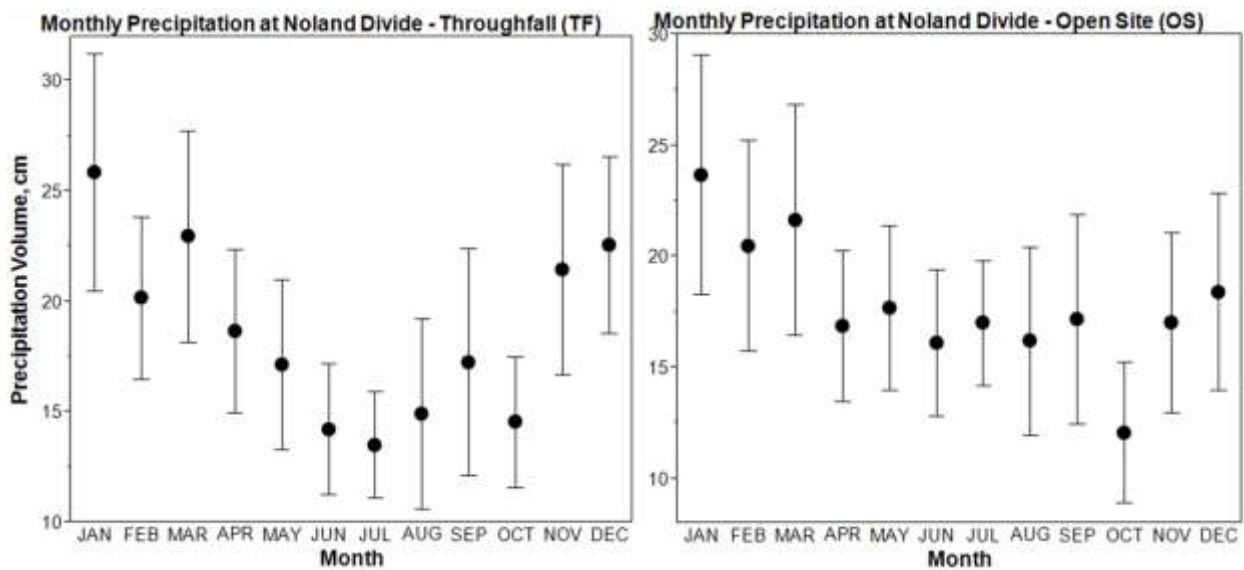


Figure 3. Distribution of monthly precipitation totals, averaged over all years (1991 to present). Error bars represent 95% confidence intervals for the mean precipitation depth (in centimeters).

2.3.2 Precipitation pH Profile

The seminal chemistry parameter for acidification is pH. The pH of precipitation, soil water, and stream water are measured and evaluated as part of the GRSM monitoring program.

Summarizing pH over spatial or temporal scales involves calculating mean values; however, the concept of “mean pH” is not trivial for a parameter that quantifies proton concentrations that vary geometrically (i.e., in powers of 10; or on a logarithmic scale). The proper method of representing the mean of a geometric parameter is to calculate the geometric mean of the parameter, but this is numerically equivalent to taking the arithmetic mean of the log-transformed value. pH is the log-transformation of the proton concentration; thus, it is appropriate to calculate the mean pH as the arithmetic mean of the pH values (Helsel 1984). This is the method used on the GRSM pH data.

Average annual pH of both TF and OS precipitation since 1991 is shown in Figure 4. Precipitation pH collected at NDW has increased from the initial lows of 4.0 and 4.4 in TF and OS, respectively, (1991), to their current levels. Since 2007, the pH of TF and OS precipitation has increased significantly. Between 1991 and 2011, the average pH of TF has been lower than the pH of OS by half-pH unit (on average), but the spread in average monthly pH values results in some overlap in year-to-year averages. Since then, a curious convergence of pH levels has occurred, suggesting that the depositional chemistry that had been causing the pH-differential in prior years may be changing in recent years.

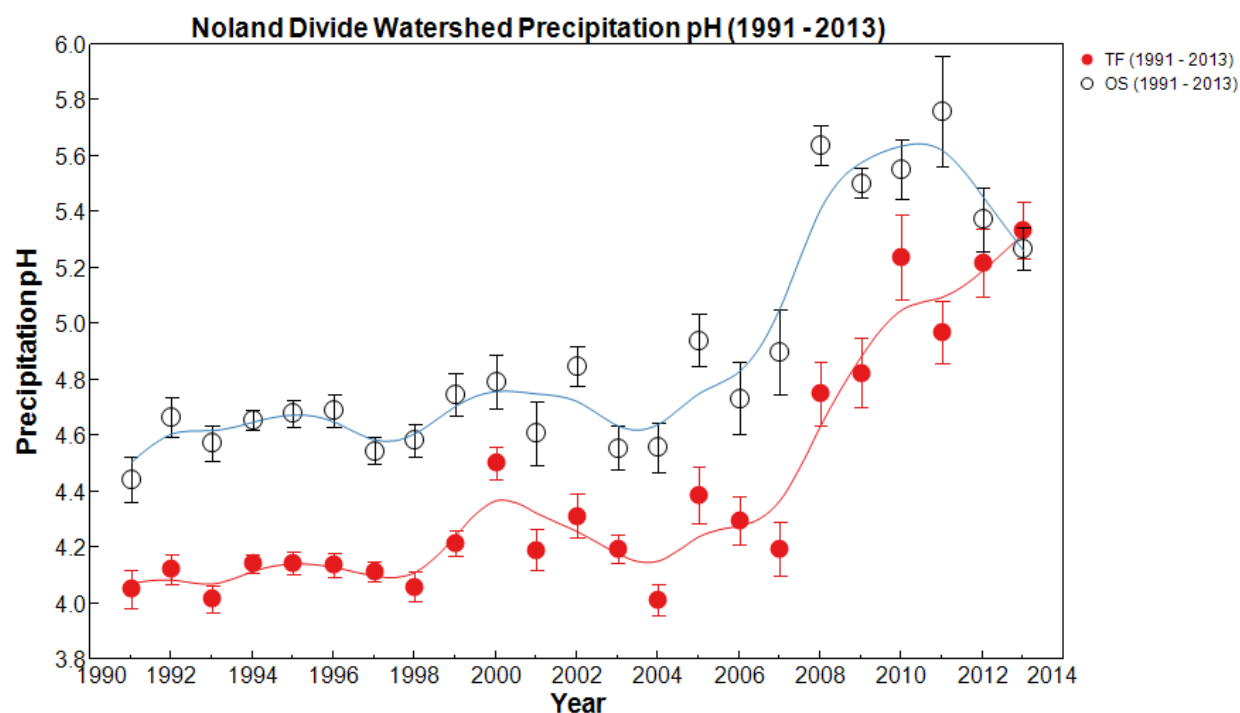


Figure 4. Annual mean pH of precipitation collected at TF (solid circles) and OS (open circles), shown with standard error bars. Data were collected between 1991 (partial year) and 2013.

In 2013, the average pH of all TF samples was 5.34, and the pH of individual TF samples ranged between 4.57 (December 2013) to 5.93 (September 2013). Over the period of record, the 2013 pH data for TF represented the highest annual average pH, the highest monthly minimum pH,

and the highest monthly maximum pH, to date. The average pH of all OS samples was 5.27, and the pH of individual OS samples ranged from 5.00 (August 2013) to 5.88 (October 2013). Over the period of record, the 2013 pH data for OS represent the sixth highest annual average pH, the third highest monthly minimum pH, and the fifth highest monthly maximum pH, to date.

2.4 Annual Deposition Rates for Chemical Constituents

Annual rates of deposition (mass equivalents per hectare per year; eq/ha/yr) of sulfur and nitrogen species into the NDW were computed for both TF and OS. Data for all years of study, including 2013, are summarized below to indicate possible trends in the long-term deposition into NDW.

2.4.1 Sulfate Deposition Profile

During 2013, the deposition of sulfate at the TF site was estimated to be 695 eq/ha/yr, and 232 eq/ha/yr at the OS site (Figure 5). These deposition rates were the fourth lowest amount measured at TF and the second lowest amount measured at OS, during the period of record. Deposition is highly dependent on rainfall volumes; i.e., mass of pollutants collected through precipitation during drought years will be less than during wet years. However, despite annual precipitation amounts remaining fairly constant since 2007-2008, the five lowest measured sulfate deposition rates at TF have been recorded in that same period of time. Thus, this deposition trend likely was being caused by decreased pollutant loadings in the atmosphere. Correlations between pollutant deposition into NDW and annual mass of sulfate/nitrate air-emissions from regional power plants, showing this influence, are presented in Section 2.7.

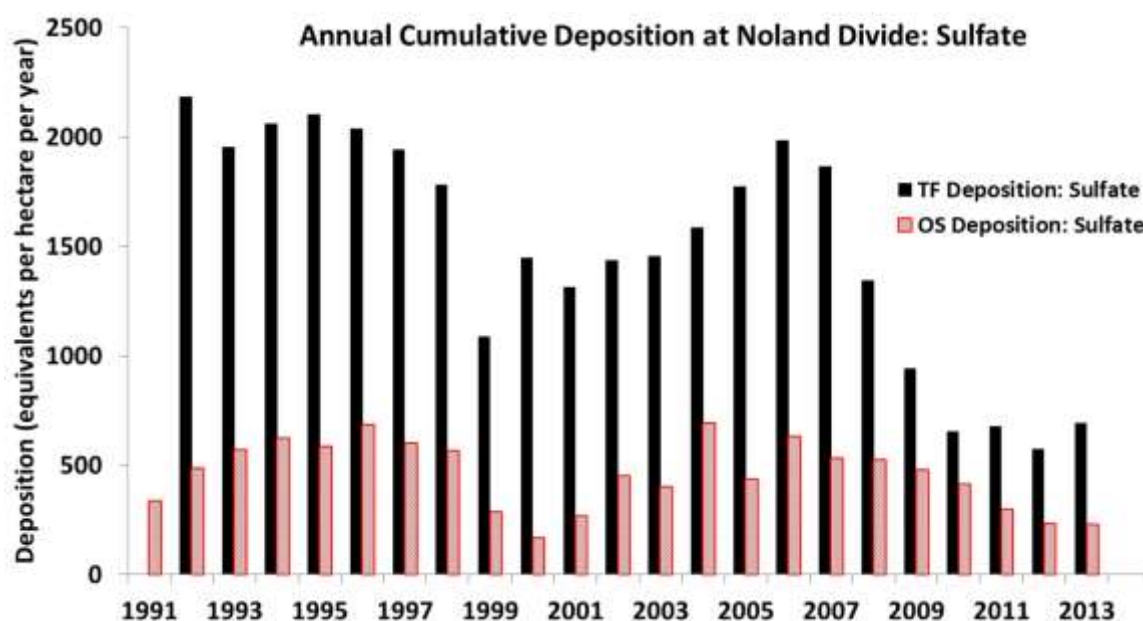


Figure 5. Total sulfate (in equivalents per hectare per year; eq/ha/yr) entering NDW via precipitation measured at TF and OS. Sampling in 1991 began mid-year; those data do not represent the entire year.

2.4.2 Nitrogen Deposition Profile

During 2013, the estimated deposition rate of inorganic nitrogen (T.I.N.) (mass per unit area) into the NDW was 344 eq/ha/yr from TF and 81 eq/ha/yr from OS (wet-only) precipitation (Figure 6). These rates were the lowest recorded at NDW, excluding the initial partial year of data collection (1991). For OS, the 2013 deposition continues a generally decreasing trend in deposited T.I.N. mass that started roughly in 2007-2008.

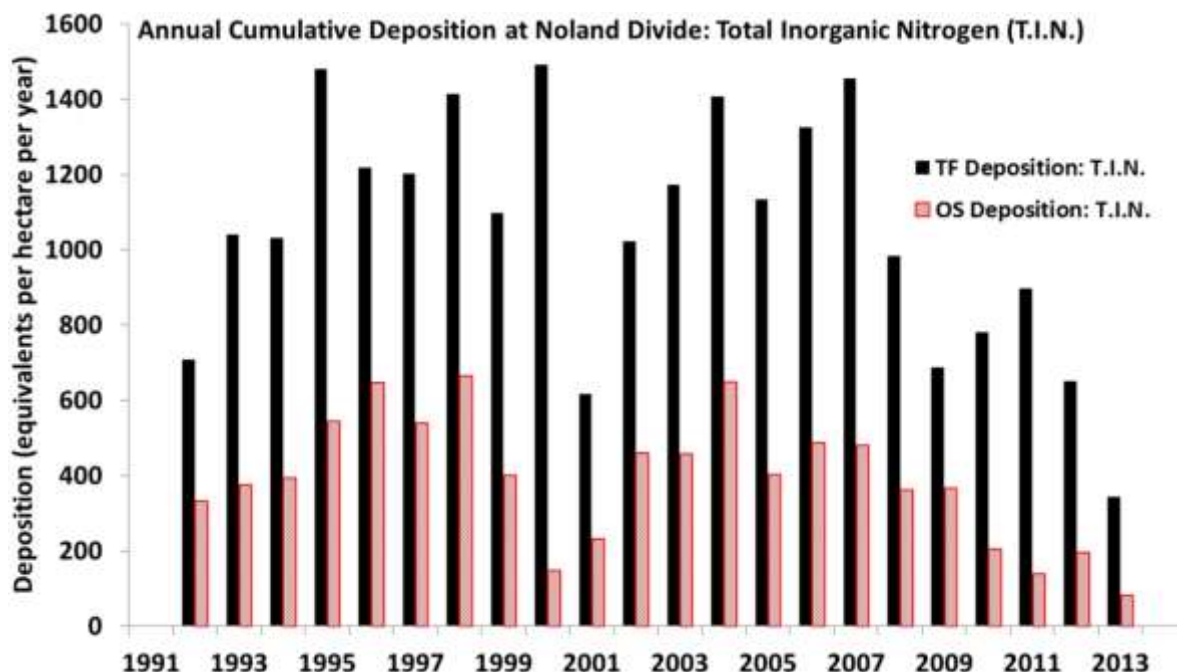


Figure 6. Total inorganic nitrogen (nitrate + ammonium; eq/ha/yr) entering NDW via precipitation measured at TF and OS. Sampling in 1991 began mid-year; those data do not represent the entire year.

2.4.3 Nitrogen Speciation Shift

Closer inspection of the nitrogen deposition data revealed an interesting relationship in the nitrogen speciation over time. In the NDW monitoring program, T.I.N. is the sum of nitrate and ammonium concentrations. Using TF data, the percentage of ammonium in the cumulative annual T.I.N. deposition was plotted over the period of record overlaid with the average annual pH of TF precipitation (Figure 7). Ammonium fraction of T.I.N. and the pH of TF precipitation appeared to be temporally correlated per visual inspection where the ratio of ammonium-to-nitrate increases with TF precipitation pH. More investigation is needed to confirm this relationship and to propose plausible explanations. Also, it can be inferred from equilibrium chemistry principles that the ratio of ammonium (ionized) to ammonia (un-ionized) concentrations in TF samples will be influenced by the precipitation pH, with ammonium predominating at lower pH conditions.

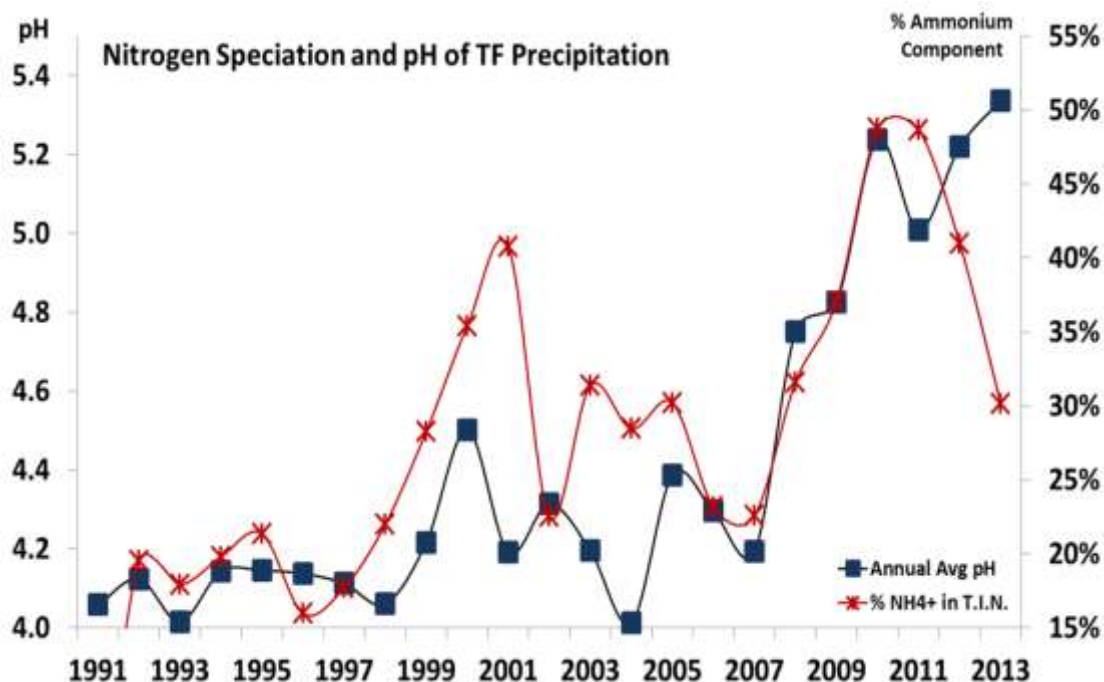


Figure 5. Annual mean percentage of ammonium in T.I.N. in TF precipitation, and the corresponding annual mean pH. Left axis is pH; right axis is percent ammonium in T.I.N. Sampling in 1991 began mid-year; that year's data do not represent the entire year.

2.5 Soil Water Chemistry

Soil water samples were collected monthly from lysimeters placed at three depths: A horizon at 8 cm (upper); Bw horizon at 35 cm (middle); and Cb horizon at 65 cm (lower). Total soil water volumes collected in 2013 were 2,340 milliliters (mL), 3,870 mL, and 11,320 mL from the upper, middle, and lower lysimeters, respectively. Soil water chemistry data for 2013 and all prior years are summarized in Table 1. In all three soil horizons, the mean 2013 soil water pH was greater than the corresponding overall mean pH for all prior years. The trend of increasing pH with depth below surface is in part due to higher organic-matter content and microbiological activity in surface soil (EPA 2002; Van Miegroet and Cole 1984). Except for sodium in the middle (Bw) horizon, mean concentrations of electrolytes in 2013 were less than corresponding mean values over all prior years. Anion concentrations did not appear to vary much with soil depth; calculated means were within the range of individual sample measurements. The same was observed for base cation concentrations in the soil water at the three soil horizons.

Table 1. Summary data statistics for conductivity, pH, common anions and base cations in soil lysimeter samples collected in 2013 and in all prior years.

Chemistry *	Year(s) and Statistics	Upper = A horizon	Middle = Bw horizon	Lower = Cb horizon
Conductivity	2013 Mean (SE)	21.3 (0.15)	26.2 (3.9)	21.3 (0.90)
	1991-2012 Mean (SE)	63.9 (2.6)	39.3 (1.4)	33.4 (0.70)
pH	2013 Mean (SE)	4.51 (0.13)	4.59 (0.11)	4.71 (0.10)
	1991-2012 Mean (SE)	4.04 (0.02)	4.36 (0.02)	4.49 (0.01)
ANC	2013 Mean (SE)	-33.8 (8.0)	-16.5 (7.2)	-20.0 (5.7)
	2005-2012** Mean (SE)	-10.9 (2.6)	-18.4 (1.6)	-25.4 (1.9)
Chloride	2013 Mean (SE)	10.9 (1.4)	19.9 (5.6)	12.0 (1.4)
	1991-2012 Mean (SE)	28.4 (2.3)	27.9 (1.9)	23.4 (1.7)
Nitrate	2013 Mean (SE)	27.1 (12.6)	39.4 (9.5)	42.9 (3.9)
	1991-2012 Mean (SE)	136.7 (10.6)	73.2 (4.4)	82.3 (3.7)
Sulfate	2013 Mean (SE)	49.3 (2.0)	82.5 (15.3)	68.5 (4.7)
	1991-2012 Mean (SE)	91.2 (3.3)	95.1 (2.4)	89.6 (1.6)
Sodium	2013 Mean (SE)	13.6 (0.84)	23.3 (6.1)	16.2 (0.93)
	1991-2012 Mean (SE)	26.2 (3.4)	24.3 (0.92)	19.8 (0.68)
Potassium	2013 Mean (SE)	7.66 (1.3)	7.96 (1.3)	6.84 (0.4)
	1991-2012 Mean (SE)	22.3 (1.6)	11.1 (1.1)	9.87 (0.93)
Magnesium	2013 Mean (SE)	15.0 (1.3)	14.0 (3.0)	15.0 (0.47)
	1991-2012 Mean (SE)	26.5 (3.3)	20.2 (0.58)	23.9 (0.67)
Calcium	2013 Mean (SE)	26.8 (5.5)	16.0 (2.8)	28.0 (3.7)
	1991-2012 Mean (SE)	50.9 (7.6)	26.9 (1.1)	38.8 (2.3)

* Conductivity in micro-siemens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter ($\mu\text{eq}/\text{L}$)

** Acid-neutralizing capacity (ANC) was added to the analytical suite for this project in 2005.

SE = standard error of the mean value.

2.6 Stream Water Chemistry

NDW stream water samples were collected from the SW and NE streamlets throughout 2013; a few collection trips were cancelled due to extreme winter conditions. Eighteen water samples were collected from each streamlet in 2013. The acidity profile of NE showed a fairly consistent pH and ANC over the year based on the reported range indicating minimal seasonal patterns in water chemistry (Table 2), although Cai et al. (2011b) found seasonal patterns mostly with stream nitrate and pH. In the SW streamlet, the same was observed: both stream pH and ANC are fairly consistent throughout the year. Comparing the two streamlets, NE stream water had lower pH and ANC, and higher dissolved solute concentrations, than the SW streamlet. The means were tested for significance, and it was found that confidence intervals of each streamlet's mean ANC did not overlap at $\alpha = 0.05$ (NE = 7.67 – 15.21; SW = 16.16 – 24.39) but did overlap at $\alpha = 0.01$ (NE = 6.24 – 16.63; SW = 14.61 – 25.94), indicating statistically significant different annual mean ANC at the 95% confidence level ($p = 0.002$). This difference between NE and SW

ANC has been observed in ANC data from prior years. The same significance test of means for streamlet pH *did not* suggest statistically significant differences in pH at $\alpha = 0.05$, although the pH in SW was consistently 0.2 pH units greater than pH in NE. In general, annual mean of most water chemistry parameters in 2013 were similar to overall mean values for pre-2013 data.

Table 2. Summary data statistics for conductivity, pH, common anions and base cations in streamlet water samples (NE and SW) collected in 2013 and in all prior years.

Chemistry *	Year(s) and Statistics	NE Streamlet	SW Streamlet
Conductivity	2013 Mean (SE)	12.9 (0.27)	11.4 (0.39)
	1991-2012 Mean (SE)	14.8 (0.08)	12.9 (0.13)
pH	2013 Mean (SE)	5.81 (0.06)	6.01 (0.07)
	1991-2012 Mean (SE)	5.61 (0.01)	5.86 (0.01)
ANC	2013 Mean (SE)	11.4 (1.8)	20.3 (1.9)
	2005-2012** Mean (SE)	4.34 (0.24)	11.7 (0.27)
Chloride	2013 Mean (SE)	16.3 (1.1)	13.2 (1.0)
	1991-2012 Mean (SE)	18.0 (0.38)	15.3 (0.37)
Nitrate	2013 Mean (SE)	21.7 (0.72)	18.3 (1.3)
	1991-2012 Mean (SE)	44.4 (0.35)	39.1 (0.32)
Sulfate	2013 Mean (SE)	47.4 (0.79)	38.5 (0.73)
	1991-2012 Mean (SE)	41.3 (0.26)	30.2 (0.21)
Sodium	2013 Mean (SE)	24.7 (0.89)	23.1 (0.37)
	1991-2012 Mean (SE)	25.4 (0.24)	25.4 (0.20)
Potassium	2013 Mean (SE)	10.6 (0.63)	7.21 (0.38)
	1991-2012 Mean (SE)	11.4 (0.26)	8.67 (0.20)
Magnesium	2013 Mean (SE)	17.5 (0.46)	16.2 (0.56)
	1991-2012 Mean (SE)	20.1 (0.16)	17.8 (0.15)
Calcium	2013 Mean (SE)	43.8 (1.3)	42.7 (1.3)
	1991-2012 Mean (SE)	50.9 (0.37)	46.2 (0.29)

* Conductivity in micro-siemens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter ($\mu\text{eq}/\text{L}$)

** Acid-neutralizing capacity (ANC) was added to the analytical suite for this project in 2005.

SE = standard error of the mean value

2.7 Atmospheric Source / Deposition Correlations

Acid-forming pollutants are transported to the GRSM by prevailing wind currents arriving from several regional and national air-borne pollutant sources. Examples of local/regional sources include Tennessee Valley Authority (TVA) fossil fuel power plants located within 100 miles of GRSM. TVA has implemented pollutant reduction measures over the years, including operational changes in the 2003-2004 and air pollution controls in 2008-2009 (TVA 2013). Data from the NDW monitoring program was used to assess whether GRSM biogeochemistry has responded to the reductions in sulfate and T.I.N. emissions. TF was used for comparison

because it represents the total deposition (both wet and dry forms). The assessment period covered in the dataset spans 1992 – 2013; 1991 was excluded because data were not collected for the entire year. Emissions data are from TVA, published annual emission estimates for sulfur as sulfur dioxide and for nitrogen as NO_x, both in units of 1000 tons per year. The emissions values represent the sum of emissions from the Bull Run and Kingston Power Plants.

Two graphs, one for sulfur equivalents and one for nitrogen equivalents, are presented which summarize temporal trends in air pollutant emissions from local coal-fired power plants, and in the deposition mass at TF (Figures 8 and 9). Sulfate TF deposition at NDW was strongly and directly correlated to amounts of atmospheric sulfur emitted from regional air pollution point sources from TVA's Bull Run and Kingston Power Plants (Figure 8). After 2008, power plant emissions drastically reduced by an order of magnitude, and correspondingly TF deposition at NDW. Both emissions and TF deposition loadings remain significantly lower through 2013 compared with loads from years prior to 2008. Although other factors and sources contribute and affect the deposition of air pollutants at the Park, it is clear that pollutants in the atmosphere have a direct effect on biogeochemistry on the ground in the GRSM.

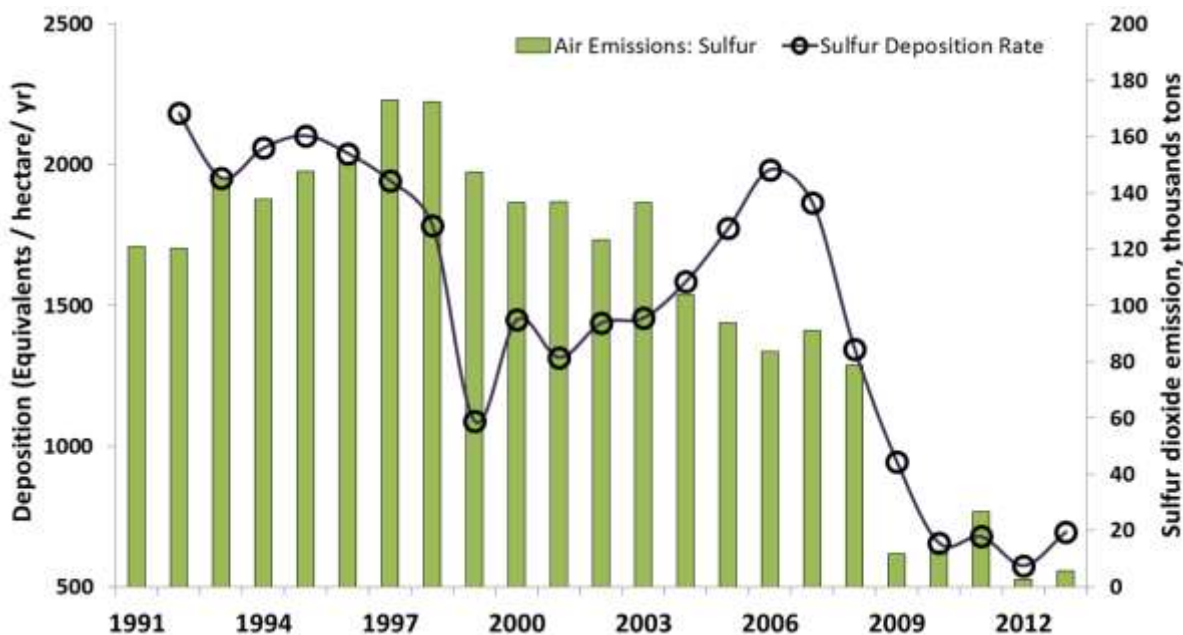


Figure 6. Correlation between mass of sulfur (tons x 1000) emitted from regional fossil fuel power plants and the annual total equivalents of sulfur per hectare deposited at the TF site. Data for the initial (partial) year 1991 are excluded.

Inorganic nitrogen deposition (quantified as T.I.N.) at TF was compared to amounts of atmospheric nitrogen emitted from regional air pollution point sources from TVA's Bull Run and Kingston Power Plants (Figure 9). The corresponding decrease in inorganic nitrogen deposition was not as pronounced as was the decrease in sulfate deposition. This is likely due to other pollutant sources for nitrogen, including NO_x from vehicular exhaust and NH₄⁺ from agricultural sources. In this report, trends and change points in emissions and TF deposition loadings for sulfur and nitrogen were interpreted by visual observation. A complete statistical analysis for a peer-review article of this data is planned for fall 2014.

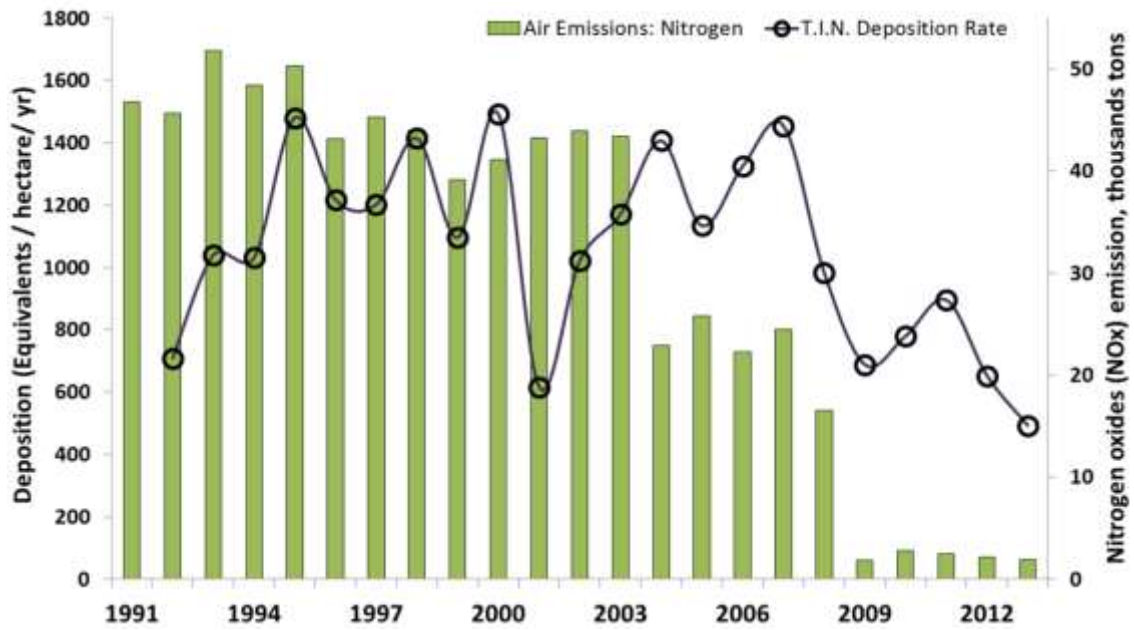


Figure 7. Correlation between mass of nitrogen (tons x 1000) emitted from regional fossil fuel power plants and the annual total equivalents of nitrogen (NO₃ + NH₄) per hectare deposited at the TF site. Data for the initial (partial) year 1991 are excluded.

3.0 Park-wide Stream Survey

Park-wide stream survey (also termed long-term synoptic stream WQ monitoring) began in October 1993 to monitor water quality in GRSM streams, and simultaneously assess possible correlations between GRSM water chemistry and atmospheric sources of acid-generating pollutants. Currently active sampling sites are distributed among seven watershed drainage basins identified by their predominant surface water body (Figure 10): Abrams Creek (4 sites); Cataloochee Creek (8 sites); Cosby Creek (4); Little River (3); Oconaluftee River (5); Road Prong/Rt.6 (8); and Hazel Creek (11). In 2013, 197 samples were collected from these locations and analyzed for chemical parameters. These seven drainage basins were selected to best represent the natural spatial variability in elevation, geology types, and land use/disturbance histories found in the GRSM (Odom 2003). Location information for these sites is listed in Appendix C.

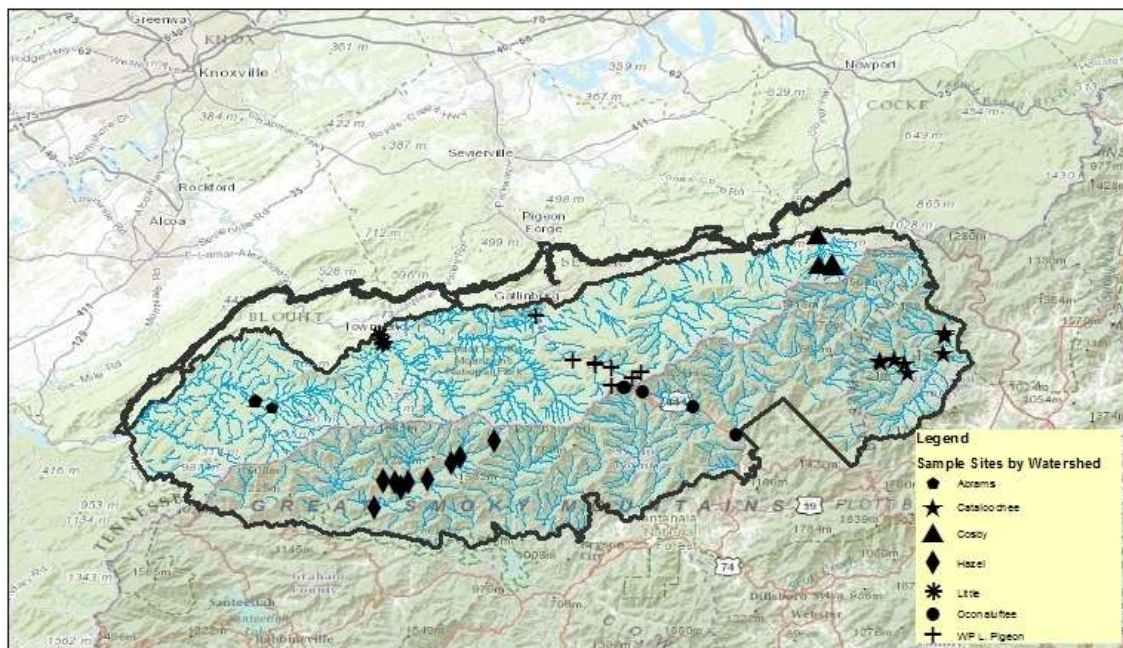


Figure 8. Currently sampled sites for the GRSM Park-wide stream survey water quality monitoring program. “WP L. Pigeon” includes Walker Prong, West Prong, and Road Prong as well as the West Prong of the Little Pigeon.

3.1 Park-Wide Water Chemistry: Watershed Summary

The water chemistry dataset of the GRSM monitoring program was evaluated for trends and correlations. The combined Park-wide water chemistry dataset has been assessed for patterns and trends (e.g., Robinson et al. 2008), but the high degree of variability observed in the combined dataset limited what conclusions could be drawn from that assessment. With growing awareness of the influence of basin-specific factors on WQ (Neff et al. 2013), the WQ dataset was reorganized and evaluated by watershed (drainage basin). This approach revealed patterns and trends in stream water chemistries throughout the GRSM. Summary statistics were calculated for all 43 sampling sites, within their corresponding drainage basin. Mean and standard error (in parentheses) over the period of record were calculated for: conductivity

(“Cond.”; $\mu\text{S}/\text{cm}$), pH (standard units), acid-neutralizing capacity ANC ($\mu\text{eq}/\text{L}$), sum of major anions ($\mu\text{eq}/\text{L}$; chloride, nitrate, sulfate), sum of base cations ($\mu\text{eq}/\text{L}$), and total inorganic solutes (TIS; $\mu\text{eq}/\text{L}$). The results are shown in Table 3.

Table 3. Selected water chemistry for 2013 and all prior years, organized by drainage basins (standard error of the mean in parentheses). Note: Abrams Creek drainage basin is divided into two subsets, Mill Creek sampling sites and Main Stem sampling sites.

Drainage Basin (Data Years)	Cond. $\mu\text{S}/\text{cm}$	pH	ANC $\mu\text{eq}/\text{L}$	$\Sigma(\text{anions})$ $\mu\text{eq}/\text{L}$	$\Sigma(\text{cations})$ $\mu\text{eq}/\text{L}$	TIS $\mu\text{eq}/\text{L}$	Charge Balance
West Prong Little Pigeon River (2013)	20.4 (0.75)	6.32 (0.09)	55.6 (6.28)	115.6 (5.09)	169.3 (9.03)	340.3 (16.6)	-1.1%
(1993 – 2012)	19.7 (0.24)	6.02 (0.03)	31.0 (1.78)	120.4 (1.44)	104.8 (5.74)	257.9 (6.74)	
Cosby Creek (2013)	15.1 (0.40)	6.19 (0.05)	23.8 (2.96)	93.6 (1.93)	121.5 (4.02)	240.4 (7.76)	-3.4%
(1993 – 2012)	16.0 (0.24)	6.11 (0.02)	27.5 (1.49)	95.8 (1.61)	100.3 (4.24)	225.3 (4.77)	
Oconaluftee (2013)	24.5 (1.98)	6.33 (0.12)	57.7 (7.70)	144.3 (20.4)	210.2 (14.6)	408.8 (29.6)	-3.3%
(1993 – 2012)	27.0 (0.87)	6.16 (0.03)	45.9 (2.33)	175.9 (5.89)	153.9 (7.27)	377.0 (8.83)	
Hazel Creek (2013)	12.4 (0.62)	6.73 (0.03)	78.3 (5.58)	49.7 (4.17)	134.6 (10.0)	263.0 (15.7)	-3.8%
(1993 – 2012)	12.8 (0.25)	6.49 (0.03)	73.6 (2.07)	43.5 (1.06)	91.9 (4.84)	208.6 (5.88)	
Cataloochee (2013)	13.5 (0.50)	6.77 (0.02)	81.3 (6.51)	50.6 (5.96)	134.8 (6.52)	267.0 (14.1)	-2.4%
(1993 – 2012)	13.8 (0.17)	6.61 (0.02)	76.1 (1.62)	45.8 (0.74)	101.2 (3.43)	222.4 (4.18)	
Little River (2013)	17.4 (0.96)	6.82 (0.03)	109.9 (9.54)	52.6 (1.55)	176.3 (12.1)	339.1 (21.5)	-5.0%
(1993 – 2012)	18.9 (0.44)	6.73 (0.03)	114.7 (4.53)	60.9 (1.03)	138.8 (6.94)	314.9 (9.41)	
ABR Mill (2013)	12.7 (0.80)	6.63 (0.04)	72.4 (8.83)	45.5 (0.76)	127.0 (7.06)	245.4 (14.4)	-5.2%
(1993 – 2012)	18.4 (1.10)	6.62 (0.03)	115.9 (12.0)	54.7 (1.36)	140.4 (12.2)	307.9 (23.1)	
ABR Main (2013)	96.7 (9.37)	7.71 (0.05)	1014.7 (108)	75.0 (3.47)	1067.1 (98.6)	2156.9 (209)	0.9%
(1993 – 2012)	95.3 (3.46)	7.48 (0.04)	940.2 (35.8)	82.2 (1.43)	688.5 (50.9)	1701.4 (69.0)	

Notes: Cond. = conductivity; ABR = Abrams Creek; ANC = acid-neutralizing capacity; TIS = total inorganic solutes

* Distribution of individual measurements shows bimodal distribution. Subsets of sites within the drainage basin have substantially different mean conductivity, pH and/or ANC.

Initially, data from all sampling sites within the Abrams Creek drainage basin were summarized together. On closer inspection, clear differences in water chemistry of individual sites warranted subdividing the Abrams Creek sites into Mill Creek (ABR Mill; Sites 173 and 488) and Abrams Creek (ABR Main; Sites 174 and 489). In the 2013 sampling period, overall ion charge balance within each drainage basin was excellent (within 5.2%) for all eight drainage basins. All except Abrams Creek were slightly imbalanced to the negative, indicating the existence of one or more anions not accounted for by the analyses applied to these samples (e.g., phosphate, carbonate, organic acids, etc.). For most parameters, the levels observed in Abrams Creek sites far exceed

those in the Mill Creek tributary sites, and in all other drainage basins. The positive ion imbalance (i.e., excess anions) and high dissolved solids content in Abrams Creek can be explained by the dissolution of limestone-karst minerals from the surrounding soil and bedrock underlying this part of the Park.

Collectively at the drainage-basin scale, the 2013 mean pH in all eight drainage basins was greater than, or equal to, the overall mean pH for all prior years. Corresponding to pH shifts, mean ANC in five drainage basins was greater than the mean ANC over all prior years. The mean concentrations of total dissolved ions in 2013, as reflected in total anions, total cations and total inorganic solutes, were greater than the overall mean concentration over all prior years in seven of the eight drainage basins (all except Mill Creek). The largest difference between 2013 mean and “all prior years” mean was in the main Abrams Creek drainage basin, the one that is highly influenced by the underlying limestone-karst minerals.

3.3.1 Abrams Creek Water Chemistry

Abrams Creek WQ data associated with four sampling locations (Sites 173, 174, 488 and 489) were available back to the beginning of the monitoring program (1993). As described earlier (Table 3), water chemistry of the four active Abrams Creek sampling sites were markedly different from all other monitored drainage basins, and closer evaluation of the data revealed clear differences among individual sites within the drainage basin. Table 4 summarizes the mean values (for current year and for all prior years) of water chemistry parameters for the four sampling sites, as well as each site’s elevation in meters above mean sea level (m amsl).

Table 4. Summary of water chemistry data for Abrams Creek sampling sites. Current year (2013) and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Mill Creek sites							
Site 173 (2013)	14.2 (1.14)	6.75 (0.03)	87.2 (12.5)	45.0 (0.96)	144.0 (9.67)	276.4 (21.4)	522.7
(1993 – 2012)	23.8 (2.02)	6.78 (0.03)	177.6 (22.5)	55.4 (1.67)	195.6 (24.0)	420.4 (45.9)	
Site 488 (2013)	11.3 (0.79)	6.50 (0.03)	57.7 (9.99)	46.1 (1.21)	110.0 (3.10)	214.4 (8.79)	545.6
(1993 – 2012)	12.0 (0.16)	6.43 (0.02)	46.0 (1.21)	54.2 (1.44)	98.3 (3.03)	198.7 (4.08)	
Abrams Creek sites							
Site 174 (2013)	97.4 (14.5)	7.72 (0.08)	1031.3 (166)	73.9 (4.78)	1082.2 (153)	2187.4 (323)	522.7
(1993 – 2012)	100.4 (4.19)	7.46 (0.05)	990.8 (44.6)	84.2 (1.63)	750.0 (60.0)	1817.9 (88.7)	
Site 489 (2013)	96.1 (13.3)	7.70 (0.07)	998.1 (154)	76.1 (5.44)	1052.0 (139)	2126.4 (298)	521.2
(1993 – 2012)	87.5 (3.24)	7.50 (0.04)	857.6 (35.6)	80.4 (1.54)	765.9 (46.2)	1692.3 (69.0)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

Water chemistry from the upper reach of Abrams Creek was distinct from all other monitored locations in the GRSM. Sites 174 and 489 had the highest values for all chemistry parameters except “sum of chloride, nitrate and sulfate.” These two sites were unique in having total base

cation (sum of sodium, potassium, magnesium and calcium) and total inorganic solute (TIS) concentrations in the thousands ($\mu\text{eq/L}$), ANC concentrations at $\sim 1000 \mu\text{eq/L}$, and $\text{pH} > 7.4$. With such high TIS and base cation concentrations, it is curious to note that concentrations of measured anions (chloride, nitrate and sulfate) have not increased proportionally, and in fact remain at historic levels (back to 1993). The anions compensating for the large concentrations of cations in water at these sites must consist of unquantified species, likely dominated by carbonate (which is clearly observed in raw ion chromatographs from anion analyses; *data not shown*). It is also notable that the mean pH in 2013 was substantially greater than the overall mean over all prior years, suggesting that pH continues to increase even in GRSM streams that have large amounts of native ANC. The Mill Creek tributary system feeds into the Abrams Creek, upstream of Site 489. The 2013 water chemistry at the two Mill Creek sites was similar to the overall mean chemistry over all prior years. There appears to be some difference in water chemistry between the two Mill Creek sites. With the exception of pH, all chemistry parameters in Site 173 were actually lower in 2013 as compared to the overall mean values over all prior years; stream pH was approximately equal within the measurement error. This trend was specific to Site 173 and might be evidence of biogeochemistry processes particular to the drainage area upgradient of that location. Site 489 appeared to reflect the flow-weighted dilution effect that Mill Creek has on Abrams Creek water chemistry.

3.3.2 Cataloochee Creek Water Chemistry

Cataloochee Creek WQ data for eight sampling locations (Sites 142, 143, 144, 147, 148, 149, 293 and 493) were available since 1993. Table 5 summarizes the mean values (for current year and for all prior years) of water chemistry parameters for the eight sampling sites, and lists each site's elevation (m amsl). The sites are presented in sequence from upstream to downstream. Water chemistry was relatively consistent within the drainage basin; magnitudes did not vary drastically among the eight sampling sites. Stream pH did not show any obvious spatial pattern, and the range of mean values for 2013 spanned only ~ 0.4 pH units. In all eight sites, the mean pH for 2013 was greater than the overall mean for all prior years, by as much as 0.2 pH units at some sites, indicating continued increase of stream pH in this drainage basin. In six of the eight sites, the mean ANC for 2013 was greater than the overall mean for all prior years, and in the two remaining sites, ANC for 2013 was essentially equally to prior years' overall mean ANC, within measurement variability. In all cases, the mean base cation concentrations for 2013 were greater than prior years' overall mean.

3.3.3 Cosby Creek Water Chemistry

Cosby Creek WQ data for four sampling locations (sites 4, 114, 137 and 492) were available back to program inception (1993). Table 6 summarizes the mean values for water quality parameters at the four sampling sites for the current year (2013) and for all prior years, and lists the site elevations (m amsl). The sites are located in pairs on adjacent branches of this drainage basin: Sites 4 and 137 are located in Rock Creek; Sites 492 and 114 are located on the main stem of Cosby Creek. The spatial relationships among these sites explain much of the water chemistry of associated samples. Sites 4 and 137 have similar water chemistry, and Sites 114 and 492 have similar chemistry, with respect to conductivity, pH, ANC, base cation concentrations, and TIS.

The mean pH of Rock Creek stream water was about 6.0 in 2013, which is consistent with these sites' overall mean pH for all prior years. The pH at Site 4 in 2013 is slightly less than prior years' mean pH, but these are essentially equal within the measurement variability. The mean

stream pH at sites in the main stem of Cosby Creek was 6.40 and 6.42, respectively. The mean pH at Sites 492, 114 and 137 in 2013 was greater than their overall mean pH in prior years. This indicates improving stream pH in the main stem of Cosby Creek and in the upper reaches of Rock Creek.

Table 5. Summary of water chemistry data for Cataloochee Creek sampling sites. Current year mean (2013) and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Site 142 (2013)	11.2 (0.75)	6.72 (0.03)	64.9 (3.30)	50.2 (19.9)	151.1 (35.2)	266.6 (56.8)	1005.8
(1993 – 2012)	11.1 (0.18)	6.55 (0.02)	57.5 (1.60)	38.3 (0.85)	89.5 (3.00)	185.4 (3.69)	
Site 143 (2013)	10.5 (0.72)	6.61 (0.02)	47.6 (7.47)	42.7 (1.64)	95.1 (2.78)	185.9 (11.2)	999.7
(1993 – 2012)	10.8 (0.17)	6.44 (0.03)	48.1 (1.59)	42.8 (0.75)	83.6 (2.66)	175.0 (3.25)	
Site 144 (2013)	10.8 (0.96)	6.69 (0.03)	55.9 (7.29)	37.4 (2.61)	90.4 (10.7)	184.1 (14.4)	911.4
(1993 – 2012)	11.3 (0.22)	6.50 (0.02)	53.2 (1.55)	43.2 (1.34)	89.3 (2.94)	191.0 (7.24)	
Site 493 (2013)	12.0 (0.77)	6.70 (0.03)	63.4 (6.62)	39.1 (2.13)	110.6 (4.17)	213.5 (12.0)	865.6
(1993 – 2012)	12.5 (0.29)	6.57 (0.03)	66.6 (2.28)	42.0 (1.01)	104.3 (2.92)	212.7 (4.23)	
Site 149 (2013)	14.8 (0.64)	6.86 (0.05)	90.0 (2.76)	82.2 (42.2)	144.1 (1.46)	316.6 (40.0)	777.2
(1993 – 2012)	14.6 (0.18)	6.66 (0.02)	80.7 (1.96)	46.5 (0.88)	119.7 (3.77)	246.4 (4.71)	
Site 147 (2013)	15.1 (1.04)	6.85 (0.04)	90.6 (12.3)	43.6 (2.53)	149.8 (10.8)	284.2 (21.4)	749.8
(1993 – 2012)	14.7 (0.22)	6.66 (0.02)	82.9 (2.04)	47.2 (0.94)	117.6 (4.04)	264.9 (12.4)	
Site 148 (2013)	16.8 (1.46)	6.93 (0.06)	146.7 (33.2)	50.4 (9.08)	166.8 (11.4)	364.2 (41.8)	754.4
(1993 – 2012)	17.1 (0.26)	6.81 (0.03)	122.1 (3.04)	42.0 (1.67)	152.9 (4.62)	313.7 (6.78)	
Site 293 (2013)	16.6 (1.09)	6.82 (0.03)	86.2 (7.97)	56.4 (1.27)	161.5 (7.20)	304.5 (15.0)	839.7
(1993 – 2012)	16.6 (0.17)	6.65 (0.02)	84.7 (1.85)	62.8 (1.41)	128.2 (4.57)	273.8 (5.84)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

The corresponding water chemistry parameter, ANC, shows patterns consistent with the stream pH data at these sites. The mean ANC in stream water from the Rock Creek sites were similar in magnitude (12.7 and 13.7 μeq/L), and the mean ANC at the main stem sites were similar in magnitude (35.0 and 33.8 μeq/L). The ANC at the upper Rock Creek site (137) and in the two main stem sites in 2013 was marginally greater than prior years' mean ANC, although the differences were within measurement variability. In contrast, the mean ANC at Site 4 in 2013 was less than the mean of all prior years. Similarly, the mean TIS concentrations in 2013 were greater than prior years' overall mean TIS at Sites 137, 492 and 114, but were less than prior years' overall mean at Site 4. Conversely, the mean sum-of-anions (chloride, nitrate and sulfate) in 2013 were less than prior years' mean anions concentration at Sites 137, 492 and 114, but was greater than prior years' overall mean at Site 4. It is unclear why the water chemistry is different between the two Rock Creek sampling locations. It would be interesting to explore the stream water chemistry of the main stem of Cosby Creek downstream of Site 4.

Table 6. Summary of water chemistry data for Cosby Creek sampling sites. Current year (2013) and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Site 137 (2013)	14.2 (0.27)	5.97 (0.04)	12.7 (3.44)	94.1 (1.75)	114.2 (2.01)	223.2 (3.74)	838.2
(1993 – 2012)	15.1 (0.18)	5.84 (0.02)	10.5 (0.84)	101.4 (1.49)	95.7 (3.91)	208.9 (4.71)	
Site 4 (2013)	13.0 (0.28)	5.97 (0.03)	13.7 (2.46)	81.5 (2.98)	100.1 (3.03)	197.5 (3.49)	634.0
(1993 – 2012)	13.9 (0.25)	6.04 (0.04)	32.8 (3.73)	76.4 (3.00)	98.9 (3.79)	210.3 (4.86)	
Site 492 (2013)	16.9 (0.37)	6.40 (0.03)	35.0 (4.24)	99.1 (1.74)	133.8 (8.44)	268.7 (11.6)	832.1
(1993 – 2012)	17.4 (0.29)	6.26 (0.03)	31.0 (1.22)	105.1 (1.57)	124.0 (4.75)	261.0 (5.72)	
Site 114 (2013)	16.4 (0.47)	6.42 (0.02)	33.8 (5.90)	99.7 (3.31)	137.9 (5.21)	272.2 (12.5)	765.0
(1993 – 2012)	17.2 (0.33)	6.30 (0.02)	33.4 (1.51)	104.2 (1.43)	121.2 (4.88)	258.0 (5.56)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.3.4 Little River Water Chemistry

Little River WQ data for three sampling locations (Sites 13, 23 and 24) were available since the program began in 1993. Table 7 summarizes mean values of water quality parameters in the current year (2013) and in all prior years. Identifying correlations or drawing conclusions about overall water chemistry was difficult when comparing data from only three sites. Water chemistry at Sites 13 and 23 was similar to each other but both were marginally different from Site 24. Water pH in 2013 was greater than mean pH over all prior years. Uncharacteristically, the mean ANC at all three sites in 2013 was not greater (as expected with increasing pH) but marginally *lower* than prior years' mean ANC, although the differences were well within the measurement variability. The same pattern was evident for conductivity and sum of anions (chloride, nitrate and sulfate). Other sites within this drainage basin have been sampled a few times in 1994-1996 for a one-time WQ assessment.

Table 7. Summary of water chemistry data for Little River sampling sites. Current year (2013) and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Site 13 (2013)	16.6 (0.94)	6.76 (0.03)	96.8 (15.6)	53.5 (2.70)	160.4 (8.34)	311.1 (22.3)	335.3
(1993 – 2012)	17.9 (0.36)	6.71 (0.03)	102.8 (3.81)	60.1 (1.17)	131.9 (6.15)	295.2 (7.61)	
Site 23 (2013)	15.3 (1.69)	6.75 (0.04)	95.3 (15.2)	47.1 (0.94)	148.8 (14.6)	291.6 (29.6)	350.5
(1993 – 2012)	17.4 (0.54)	6.68 (0.03)	103.4 (5.70)	57.6 (1.51)	130.9 (7.53)	292.5 (11.4)	
Site 24 (2013)	20.3 (1.76)	6.94 (0.03)	137.5 (15.0)	57.1 (2.48)	219.7 (25.2)	414.5 (40.0)	350.5
(1993 – 2012)	22.0 (0.51)	6.82 (0.03)	139.4 (4.87)	65.1 (1.06)	161.2 (7.89)	366.0 (10.4)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.3.5 Oconaluftee River Water Chemistry

The Oconaluftee River WQ dataset associated with five sampling locations (Sites 251, 252, 253, 268 and 270) included data back to 1993. Table 8 summarizes the mean values (for current year and for all prior years) of water chemistry parameters for the five sampling sites, and the site elevations. Sites are presented in upstream to downstream sequence.

Table 8. Summary of water chemistry data for Oconaluftee River sampling sites. Current year (2013) and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Site 253 (2013)	28.7 (3.48)	6.32 (0.31)	68.3 (21.3)	178.7 (41.4)	261.6 (18.9)	512.0 (37.0)	1450.8
(1993 – 2012)	25.6 (0.95)	6.56 (0.04)	86.5 (2.18)	129.8 (5.95)	176.2 (8.54)	392.5 (12.4)	
Site 252 (2013)	32.7 (3.06)	5.94 (0.31)	44.3 (20.4)	217.1 (46.4)	261.7 (18.8)	492.5 (56.4)	1426.4
(1993 – 2012)	45.2 (1.36)	5.33 (0.07)	16.0 (8.09)	325.1 (12.1)	241.9 (12.9)	618.6 (20.6)	
Site 251 (2013)	27.8 (0.89)	6.36 (0.01)	35.2 (1.90)	194.1 (4.50)	232.6 (2.83)	462.8 (8.40)	1222.2
(1993 – 2012)	29.8 (0.67)	6.15 (0.02)	24.5 (1.05)	212.8 (5.29)	188.2 (9.89)	424.7 (13.2)	
Site 270 (2013)	12.9 (0.45)	6.60 (0.04)	59.8 (3.11)	48.1 (1.49)	114.4 (3.66)	222.8 (4.76)	666.0
(1993 – 2012)	12.3 (0.17)	6.47 (0.03)	46.2 (1.60)	57.1 (1.74)	108.4 (1.52)	211.6 (3.28)	
Site 268 (2013)	14.4 (0.80)	6.61 (0.03)	82.4 (4.72)	48.3 (1.27)	129.2 (3.78)	260.4 (6.90)	666.0
(1993 – 2012)	13.9 (0.21)	6.51 (0.02)	61.3 (2.09)	60.3 (1.84)	104.6 (4.16)	226.3 (4.81)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

Stream chemistry in this drainage basin showed strong spatial trends, with higher concentrations of total dissolved solutes and lower pH and ANC at the upstream sites (253, 252, 251) than at the downstream sites (270 and 268). It is suspected that water chemistry at Site 253, which is immediately up-gradient of Site 252, is influenced by runoff from an adjacent parking area. However, the general trend in water chemistry is decreasing concentrations and increasing pH with distance downstream, suggesting a dilution and buffering effect by tributaries feeding the main stem.

The predominance of solutes leached from soil and bedrock in this drainage basin originates from sources near the headwaters. Samples collected from Site 252 in 2013 had the highest aluminum (0.120 micromoles per liter; μM), copper (0.0012 μM), manganese (0.113 μM), and zinc (0.043 μM) concentrations.

3.3.6 West Prong of the Little Pigeon River Water Chemistry

Eight sampling locations within the West Prong of the Little Pigeon River (WPLPR) drainage basin (Sites 30, 66, 71, 73, 74, 233, 234 and 237) have been monitored since 1993. Table 9 summarizes mean values of water quality parameters in the current year (2013) and in all prior years. The table is organized to group sites within individual WPLPR reaches, where sites 237, 233, 74 and 73 are in Walker Camp Prong, sites 234 and 71 are in Road Prong, and sites 66 and 30 are in the WPLPR main stem, downstream of the confluence of the other two prongs.

Table 9. Summary of water chemistry data for West Prong of Little Pigeon River sampling sites. Current year (2013) and mean of all prior years (standard error of the mean is shown in parentheses). Data organized by river-reach: Walker Camp Prong and Road Prong merge just downstream of Sites 73 and 71, and continue as West Prong of Little Pigeon River.

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Walker Camp Prong							
Site 237 (2013)	16.3 (0.59)	4.97 (0.05)	-8.96 (2.46)	99.2 (4.59)	88.9 (3.93)	201.2 (7.74)	1377.7
(1993 – 2012)	19.8 (0.25)	4.87 (0.03)	-12.6 (0.90)	123.2 (2.20)	80.9 (4.48)	223.7 (6.05)	
Site 233 (2013)	25.0 (0.81)	6.55 (0.13)	64.7 (8.56)	142.9 (2.40)	222.5 (12.4)	430.9 (17.6)	1296.9
(1993 – 2012)	24.3 (0.35)	6.17 (0.05)	34.4 (2.84)	156.9 (1.82)	151.2 (9.14)	343.4 (11.2)	
Site 74 (2013)	27.4 (1.38)	6.79 (0.04)	107.6 (17.4)	137.3 (4.90)	235.4 (16.4)	480.6 (34.7)	1164.36
(1993 – 2012)	25.6 (0.43)	6.51 (0.04)	69.1 (3.90)	142.1 (1.84)	164.0 (10.3)	375.6 (12.9)	
Site 73 (2013)	21.8 (1.27)	6.59 (0.03)	66.8 (13.8)	123.8 (4.42)	166.8 (34.8)	357.8 (48.4)	1024.1
(1993 – 2012)	21.0 (0.33)	6.32 (0.03)	38.4 (2.43)	130.7 (1.91)	130.6 (7.58)	300.6 (9.10)	
Road Prong							
Site 234 (2013)	14.3 (0.52)	6.08 (0.04)	19.9 (2.45)	116.2 (33.4)	110.8 (4.62)	248.7 (38.7)	1524
(1993 – 2012)	15.2 (0.17)	5.89 (0.03)	16.6 (1.17)	100.2 (1.19)	95.8 (4.37)	212.0 (5.17)	
Site 71 (2013)	15.0 (0.57)	6.37 (0.07)	46.1 (5.15)	79.4 (1.84)	140.6 (17.3)	235.3 (18.1)	1036.6
(1993 – 2012)	16.3 (0.31)	6.19 (0.03)	30.4 (2.18)	98.9 (2.25)	108.0 (5.51)	236.4 (7.30)	
W. Prong Little Pigeon River							
Site 66 (2013)	19.3 (0.84)	6.54 (0.04)	54.3 (6.10)	110.7 (2.55)	179.6 (8.65)	345.2 (15.1)	816.9
(1993 – 2012)	20.4 (0.38)	6.33 (0.03)	39.4 (1.98)	121.4 (1.53)	129.1 (7.19)	290.9 (8.09)	
Site 30 (2013)	21.0 (0.56)	6.67 (0.03)	89.5 (8.49)	97.3 (1.84)	200.6 (5.06)	387.8 (11.6)	435.9
(1993 – 2012)	20.9 (0.21)	6.50 (0.03)	63.0 (2.50)	112.3 (1.86)	141.3 (7.40)	314.6 (8.69)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

Without exception, mean pH and ANC concentrations in 2013 samples were greater than the overall mean values for all prior years. Stream chemistry in the WPLPR shows strong spatial trends. The clearest trend is seen in the Walker Camp Prong – WPLPR basin; pH and ANC start at levels consistent with severe stream acidification (Site 237: pH < 5; ANC < 0 μeq/L) and increase with distance downstream. The initial acid conditions in this small headwater reach of Walker Camp Prong were in part due to oxidation of reduced-sulfur (pyritic) minerals in Anakeesta Formation bedrock, which is exposed to the atmosphere at several locations throughout this region. The oxidation of sulfide to sulfate can generate a large amount of acidity as a by-product, resulting in sulfuric acid leaching into soil water and migrating into drainage channels and creeks.

Of special note was the sharp increase in pH and ANC (and in dissolved solids) between Sites 237 and 233. This can be attributed to residue from dolomitic chat that is applied to road surfaces in this watershed during winter driving conditions (NPS, *pers. comm.*). The carbonate mineral content of this road treatment disperses and migrates into the creek system in the Site 233/234 area, and neutralizes the acidity introduced into the creek water from upstream sources. Also note the slight decrease in pH and ANC observed between Site 74 and Site 73. Located between these two sites is the confluence of an unnamed tributary originating from the Alum Cave area of this watershed. The Alum Cave region of the park also has exposed Anakeesta Formation bedrock, which is susceptible to oxidation and formation of acidity, just as at the headwaters of the Walker Camp Prong. The leached sulfuric acid migrates into that unnamed tributary, which mixes at the confluence with the “treated” stream water from Walker Camp Prong. The mixture resulted in a slight depression in pH and ANC, but the effect was localized and is neutralized by the confluence with Road Prong water further downstream.

Similar spatial patterns were seen in the Road Prong – WPLPR basin. Stream pH and ANC go from relatively low values (Site 234: pH 6.1 and ANC ~20 ueq/L) to larger values further downstream (Site 30: pH 6.7 and ANC ~90 µeq/L). Solute concentrations (as reflected in conductivity and TIS data) increase with distance downstream, which is common in watersheds that accrue dissolved solutes from weathering minerals throughout the expanding drainage area. Solutes in Road Prong may not originate from one point-source (e.g., bedrock oxidation at headwaters), but from natural geologic weathering throughout the drainage area. An observation to note for this stream branch was the relatively larger ion charge imbalance in 2013 samples from Sites 71 and 234, as compared to the mean ion charge imbalance in 2013 samples from the other sampling sites in this watershed.

3.3.7 Hazel Creek Water Chemistry

Eleven sites (Sites 211, 224, 310, 311, 479, 480, 481, 482, 483, 484 and 485) in Hazel Creek have been sampled for the Park-wide monitoring program (Table 10). Data for most sites were available back to 1996; Sites 221, 310 and 311 have been monitored since 1993.

Table 10 shows mean values of water quality parameters in the current year (2013) and in all prior years. Sites are organized into groups based on reach or tributary: Site 310 is in Bone Valley Creek tributary; Sites 481, 482, 483 and 480 are in a tributary here called Sugar Fork Creek; and Sites 221, 224, 485, 484, 311 and 479 are in the main stem of Hazel Creek. Stream chemistry was relatively consistent within the drainage basin; differences in the water chemistry parameters vary only slightly among the 11 sampling sites.

Table 10. Summary of water chemistry data for Hazel Creek sampling sites. Current year (2013) and mean of all prior years (standard error of the mean is shown in parentheses). Data are organized by river-reach: Bone Valley Creek and Sugar Fork Creek merge into the main stem of Hazel Creek.

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Sugar Fork Crk.							
Site 481 (2013)	16.0 (4.95)	6.80 (0.03)	101.0 (7.86)	67.3 (29.4)	147.5 (37.5)	316.1 (74.8)	774.2
(1993 – 2012)	18.3 (0.61)	6.55 (0.04)	86.3 (3.24)	78.3 (4.13)	126.6 (9.23)	289.9 (12.2)	
Site 482 (2013)	14.1 (1.60)	6.82 (0.08)	100.1 (19.8)	79.3 (33.4)	165.4 (20.2)	345.2 (33.1)	774.2
(1993 – 2012)	13.8 (0.33)	6.55 (0.04)	89.5 (3.29)	40.4 (0.97)	111.9 (6.82)	240.3 (7.66)	
Site 483 (2013)	14.1 (2.67)	6.76 (0.02)	102.2 (4.81)	44.4 (5.00)	236.8 (55.3)	383.7 (65.1)	707.1
(1993 – 2012)	14.5 (0.34)	6.59 (0.04)	86.6 (3.22)	47.3 (1.22)	112.0 (6.33)	244.6 (7.91)	
Site 480 (2013)	13.3 (1.92)	6.85 (0.03)	95.1 (15.2)	38.6 (0.31)	138.4 (3.16)	272.2 (18.7)	666.0
(1993 – 2012)	13.6 (0.36)	6.59 (0.04)	85.3 (2.62)	39.9 (1.97)	105.2 (5.97)	229.2 (7.33)	
Bone Valley Crk.							
Site 310 (2013)	12.6 (1.44)	6.81 (0.02)	87.8 (20.8)	42.4 (2.94)	151.8 (24.4)	282.3 (0.65)	682.8
(1993 – 2012)	12.7 (0.33)	6.56 (0.03)	76.7 (3.04)	41.1 (1.06)	90.2 (5.61)	207.1 (6.85)	
Walker Creek							
Site 485 (2013)	11.7 (1.88)	6.66 (0.11)	62.5 (4.83)	43.3 (8.45)	113.8 (0.54)	219.9 (4.27)	871.7
(1993 – 2012)	11.3 (0.25)	6.52 (0.04)	71.7 (3.10)	33.9 (1.15)	89.3 (5.13)	193.9 (6.49)	
Hazel Creek							
Site 221 (2013)	9.25 (1.01)	6.41 (0.07)	29.6 (4.86)	48.5 (3.86)	82.9 (3.16)	161.9 (5.69)	1219.2
(1993 – 2012)	10.5 (0.28)	6.21 (0.04)	28.9 (1.58)	57.7 (2.03)	70.2 (3.92)	157.6 (4.91)	
Site 224 (2013)	10.3 (1.42)	6.62 (0.09)	49.2 (4.31)	43.8 (3.11)	98.1 (3.11)	191.7 (4.21)	1219.2
(1993 – 2012)	10.4 (0.41)	6.38 (0.35)	42.8 (2.54)	43.8 (2.67)	98.4 (2.62)	183.4 (5.45)	
Site 484 (2013)	10.5 (1.28)	6.67 (0.03)	67.2 (5.41)	39.0 (0.48)	103.2 (1.39)	209.8 (4.52)	754.4
(1993 – 2012)	10.7 (0.24)	6.46 (0.04)	54.8 (2.62)	38.6 (1.08)	38.6 (1.08)	84.0 (4.44)	
Site 311 (2013)	12.1 (0.66)	6.80 (0.08)	92.6 (8.62)	43.0 (3.44)	123.8 (12.6)	259.8 (24.6)	656.8
(1993 – 2012)	11.9 (0.27)	6.50 (0.03)	65.7 (2.91)	40.6 (1.78)	88.6 (4.97)	194.3 (5.91)	
Site 479 (2013)	12.1 (1.11)	6.79 (0.01)	73.9 (11.2)	57.4 (14.5)	118.9 (2.71)	250.5 (23.0)	530.4
(1993 – 2012)	11.7 (0.31)	6.54 (0.04)	68.6 (2.25)	38.1 (1.39)	90.9 (5.31)	198.2 (6.68)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.4 Park-Wide Water Chemistry: Temporal Trends

Descriptive statistics for WQ parameters (minimum, maximum, mean of the median values across all Stream Survey sites, standard deviation, and coefficient of variation) measured in 2013 at the 43 survey sites have been summarized (*see* Table 4). A more detailed analysis of trends can be found in Schwartz et al. (2013).

3.5 Park-Wide Water Chemistry: Toxicological Thresholds

Schwartz et al. (2013) reviewed the literature of aquatic toxicological thresholds for pH, aluminum, and zinc. It is well documented that growth of trout species is inhibited at water pH < 5.5, and trout abundance is reduced at pH < 5.0.

3.5.1 pH

Tennessee and North Carolina State Water Quality Standards for all designated uses (domestic water supply, industrial water supply, fish and aquatic life, recreation, irrigation, and livestock watering and wildlife) specify that water pH shall not fluctuate more than 1.0 unit over a period of 24 hours and shall not be outside the ranges: 6.0 to 9.0 in wadeable streams, and 6.5 to 9.0 in larger rivers, lakes, reservoirs, and wetlands (Tennessee Department of Environment and Conservation [TDEC] General Water Quality Criteria rule 0400-40-03-.03 Criteria for Water Uses, December 2013 revision). In Tennessee, streams are classified as impaired with respect to pH when “10% or more of sample measurements do not meet the numeric water quality criteria.” Given that the basis for the “10%” requires evaluation of multiple years of pH data, it is beyond the scope of this Annual Report. Reported here are counts and samples that did not meet the designated use criterion for pH, not impairment status. The information presented here is useful for assessing stream impairment in other reports. Of the 197 Park-wide samples collected in 2013, 21 samples were non-compliant with the pH criterion (< 6.0). They were collected from only seven sites in three drainage basins:

- Site 4 in Cosby Creek (five samples; pH range = 5.87 – 5.97)
- Site 137 in Cosby Creek (three samples; pH range = 5.84 – 5.95)
- Site 253 in Oconaluftee Creek (two samples; pH = 5.46 and 5.22)
- Site 252 in Oconaluftee Creek (three samples; pH = 5.20 – 5.36)
- Site 233 in Walker Camp Prong of Little Pigeon River (one sample; pH = 5.91)
- Site 237 in Walker Camp Prong of Little Pigeon River (six samples; pH = 4.83 – 5.16)
- Site 234 in Road Prong of Little Pigeon River (one sample; pH = 5.91)

It is noted that all seven sites responsible for the non-compliances were located near exposed Anakeesta Formation bedrock, and that their water chemistry was likely strongly influenced by the pyrite oxidation/sulfuric acid leaching associated with that geology. Site 237, which is located on exposed Anakeesta Formation bedrock, alone was responsible for the most non-compliances at a single location (six), the only instances of stream pH < 5.0 in the Park (five), the lowest measured pH (4.83), and the six lowest pH values among all Park-wide samples in 2013.

3.5.2 Aluminum

The current toxicity threshold for total dissolved aluminum is 0.20 mg/L (Baldigo and Murdoch 1997). In 2013, seven samples had measured concentrations of total aluminum (analyzed by ICP) were above this criterion value; however, the toxicity of dissolved aluminum may be strongly dependent on speciation (Burns 1989). Not unexpectedly, these instances of aluminum threshold non-compliance were associated with the same locations at which pH non-compliance was determined:

- Site 137 in Cosby Creek (one sample; [aluminum; Al] = 0.33 mg/L)
- Site 253 in Oconaluftee Creek (one sample; [Al] = 0.31 mg/L)
- Site 252 in Oconaluftee Creek (two samples; [Al] = 0.25 and 0.28 mg/L)
- Site 237 in Walker Camp Prong (Little Pigeon) (two samples; [Al] = 0.21 and 0.3 mg/L)
- Site 74 in Walker Camp Prong (Little Pigeon) (one sample; [Al] = 1.46 mg/L)

It should be noted that the highest aluminum concentration was measured near the confluence with an unnamed tributary draining the Alum Cave Bluff area. The geology of this region is renowned for its unique rare-earth and oxalate mineralogy (Peacor et al. 1999; Coskren and Lauf 2000; Rouse et al. 2001), high aluminum (“Alum”) and sulfur content (Flohr et al 1995), and propensity to create acidic weathering by-products (Hammarstrom et al. 2003). The combination of pyrite oxidation, acid leaching and mineral dissolution could be one explanation for the aluminum content of samples from this location.

3.5.3 Zinc

The current toxicity threshold for total dissolved zinc is 0.219 mg/L (Cai et al. 2013). Only one sample in 2013 (Site 488; Mill Creek in the Abrams watershed system) had a non-compliant concentration of zinc (0.33 mg/L). The result is not consistent with the other chemistry of that sample (pH = 6.5; low concentrations of other trace metals and base cations) and its location within a limestone-dominated geology; however, the data quality checks for that sample do not indicate any issues that might have compromised the accuracy of that result.

4.0 Laboratory Data Quality Evaluations

Procedures for chemically analyzing samples for pH, ANC, conductivity, ions, and dissolved metals were based upon approved standard methods (Appendix B). WQ results for all samples are reported and archived in the NPSTORET database; however, data quality is reported here. In 2013, 407 water samples were analyzed: (i) NDW precipitation at OS and TF, soil lysimeter, and SW/NE stream water samples (N = 110); (ii) Park-wide Stream WQ Survey grab samples, including Hazel Creek (N = 274); and (iii) Rock Creek (N = 29).

Water samples collected in the field were transported to UTK-CEE lab and within 48 hours samples were analyzed for pH, ANC, and conductivity. Park-wide samples collected by volunteers from Trout Unlimited were taken to the GRSM WQ field refrigerator for storage. The aim is to meet the 48-hour hold time requirement, but depending on sampling timing and logistics some samples might not have been met by this criterion. Analyses for pH, conductivity and gran ANC were conducted at room temperature to standardize results among many samples collected from different locations, times, and temperatures. After completing these analyses, water samples were stored (refrigerated) for remaining analyses (i.e., ions and dissolved metals). UTK-CEE analytical instruments and procedures were optimized for low concentrations of dissolved constituents. Thus, dilution is rarely necessary for Park samples.

Precision and bias of this year's WQ data generated by this laboratory was inferred based on a number of QA procedures and special known-concentration standards and samples. These include known-concentration QC standard solutions, split sample duplicates, known-addition spiked samples, USGS certified QA solutions, and field and instrument blanks. Typical criterion for acceptable precision and bias is $\pm 20\%$ of target value (Standard Methods 1999). This year's analytical data quality evaluation results are presented below.

4.1 Ion Chromatography Data Quality

Instrument/hardware issues early in the 2013 monitoring year resulted in acquisition of new instrumentation. The old and new Dionex™ ion chromatograph system (ICS) consisted of the following components, respectively:

- Prior to November 2013: Single-channel IC system with a CD25-1 conductivity detector, an IP25 isocratic pump, and an AS50 autosampler (holding 10-mL polycarbonate sample vials and using 50 μ L injection volumes). Cation separations were obtained using a CERS-500 (4 mm) suppressor (at 100 mA current), guard and analytical columns, with methane-sulfonic acid (MSA) eluent. Anion separations were obtained using an ASRS-300 (4 mm) suppressor (100 mA current), guard and analytical columns, and internally-generated potassium hydroxide (KOH) eluent from an EG50 Eluent Generator module.
- After November 2013: Dual-channel system consisting of an ICS-1100 cation and ICS-2100 anion chromatographs, and an AS-AP autosampler (holding 2-mL sample vials and using 25 μ L injections). Cation peak separation was obtained with a CERS-500 (4 mm) suppressor (at 50 mA current), guard and analytical columns, with 16 milli-normal (mN) sulfuric acid eluent (flow rate = 1.0 milliliter per minute; mL/min). Anion separation was obtained using an ASRS-300 (4 mm) suppressor (87 mA current), guard and analytical columns, with potassium hydroxide (KOH) eluent (flow rate = 1.0 mL/min) generated internally with an eluent generation cartridge (EGC).

Samples collected early in the monitoring year, run on the old ICS, were rerun on the new ICS to ensure continuity of IC data quality for the 2013 monitoring year. DI water produced in-house was analyzed to confirm purity. Calibration curves from the instruments had coefficient of determinations (R^2) > 0.9995. Analytical limits of the IC are reported in Table 13: quantitation limits (QL); lab water blanks; and field blanks. The QL is a more realistic indicator of analytical sensitivity expected from the instrument. Analyzing laboratory water blanks with processing (method blanks) or directly from water purification unit (lab blanks) provide information on water source purity, labware cleanliness and lab technique. Field blanks provide information on field collection technique and sample handling. Also in Table 13 are reported precision of replicate field samples, and recovery efficiency of spiked field samples (“matrix spike”).

QA/QC results for IC analyses were within the acceptance criterion ($\pm 20\%$) in 2013. Field sample blanks results were near or below detection limit (Table 11). Precision of replicate analyses for chloride and nitrate was $\leq 1\%$; for ammonium, it was 9%. Repeatability of ammonium analyses are challenging because of the extremely low concentrations typically found in GRSM samples, and is compounded by the sensitivity of ammonium/ammonia equilibrium chemistry to sample pH. The higher duplicate measurement accuracy of sulfate was influenced by differences in concentrations based on vial material (glass versus plastic). All results are included in the summary results. The matrix spike recovery efficiency for the three anions and ammonium ranged between 100% and 101%.

Table 11. Ion chromatograph instrument and method QA summary (anions and cations)

QA Activity	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺
Quantitation limits (QL, mg/L)*	0.13	0.28	0.29	0.04
Concentrations in laboratory water blanks, mg/L (# samples)	0.087 (11)	0.140 (11)	0.101 (11)	< 0.04 (114)
Concentrations in field blanks, mg/L (# samples)	0.081 (28)	0.077 (28)	0.155 (28)	< 0.04 (7)
Matrix duplicate accuracy, absolute %-difference (# samples)	0.16 (46)	0.94% (46)	4.65% (46)**	1.08% (5)
Efficiency of matrix spike recovery, % (# samples)	100.3% (44)	100.9% (43)	100.3% (44)	100.9% (20)

* Reflects the lowest concentration that can be quantitated with 95% confidence. Estimated here as the upper 95% confidence interval of the mean.

** Significant differences in concentrations were found depending on IC vial material (glass versus plastic). Results reflect this variability caused by vial material.

4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry Data Quality

Major cations [sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), and calcium (Ca²⁺)] and six trace metals [aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), silicon (Si), and zinc (Zn)] were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Standards were prepared using certified ICP reagents (SPEX CertiPrep, Metuchen, NJ) and Milli-Q (Type 1) DI water (EMD MilliPore, Billerica, MA). Standard curves produced by the instrument were checked for linearity (target R^2 > 0.9999) prior to sample introduction. The

ICP-AES apparently gives non-linear detector responses to concentrations of some elements; sodium, potassium and aluminum are reported to respond in this manner.

4.2.1 Detection Limits, Field Blanks, and Laboratory (Instrument) Blanks

Instrument detection limits on the ICP-AES are within the range that is typical for this type of instrument and analytical method (Table 12). They range from 2.9 to 9.0 parts per billion (ppb; micrograms per liter). A more realistic indicator of instrument capabilities is a quantitation limit (larger than the instrument detection limit) which indicates concentrations that can be quantified with high level of confidence. Laboratory matrix blanks and field blanks were processed and analyzed to check for potential cross-contamination that might be caused by UTK-CEE lab or field methods, or by the use of contaminated materials. Analytical results for these QA samples also are presented in Table 12. Concentrations in QA blank samples were in the very low parts per billion, near or below the instrument quantitation limits. These results indicate reliable lab technique, good control from cross-contamination, and good resolution power for 2013. Field blank samples collected by volunteer groups show more variability than laboratory blanks. Sodium and silicon were detected at relatively high concentrations and with high variability in the “Z-sample” field blanks. The cause of this slight elevation in concentrations in the Z-sample field blanks is not known.

Table 12. ICP-AES detection limits and sample blank results.

Element	Detection Limits ¹ (mg/L)	N	Concentration in Matrix Blanks ² (mg/L)	N	Concentration in Field Blanks ³ (mg/L)	N
Aluminum	0.0043	101	0.0133	55	0.0141 (0.025) ⁴	28
Calcium	0.0090	101	< 0	55	0.0868 (0.041)	28
Copper	0.0029	101	0.0005	55	< 0	28
Iron	0.0040	101	0.0002	55	0.0081 (0.013)	28
Potassium	0.0043	101	< 0	55	0.0183 (0.012)	28
Magnesium	0.0071	101	0.0008	55	0.0133 (0.006)	28
Manganese	0.0031	101	< 0	55	< 0	28
Sodium	0.0030	101	0.0020	55	0.1243 (0.260)	28
Silicon	0.0046	101	< 0	55	0.2075 (0.381)	28
Zinc	0.0031	101	0.0065	55	0.0385 (0.042)	28

¹ Detection Limit = (Standard Deviation) x (Student's t @ 99% Confidence Level and sample size, N)

² Matrix blanks are 1% nitric acid solutions (ultra-pure grade) in Type 1 deionized water, prepared in lab.

³ Field blanks consist of Milli-Q (Type 1) deionized water in sample bottles, carried into the field and exposed to field conditions, and returned to lab to be processed as an ordinary sample.

⁴Standard deviation from the mean.

4.2.2 Quality Control Check (QCC) Solutions

A quality control check (QCC) standard solution was prepared from certified reagents and Milli-Q (Type 1) DI water, and run every ten samples to monitor instrument function during each run. The concentration of the QCC standard was targeted to match the low concentration standard. The measured QCC concentrations were compared to actual concentrations of the corresponding QCC solution, calculated from preparation weights and volumes. Analytical results for the QCC samples are presented in Table 13, as mean % accuracy relative to each the actual element concentrations in each QCC solution. The known-concentration quality control check (QCC) solutions were analyzed a total of 105 times this year. The bias and precision of analyses had an overall accuracy of 100.1% for all elements combined, and an overall standard error of 0.25%. All 10 elements were measured with similar accuracy; analytical accuracy ranged from 99.1% to 101.3%.

Table 13. ICP-AES accuracy (based on prepared QCC standards)

Element	N	Mean % Accuracy	Standard Error *	CV **
Aluminum	105	99.8 %	0.36 %	3.7 %
Calcium	104	101.3 %	0.32 %	3.3 %
Copper	105	99.1 %	0.22 %	2.2 %
Iron	105	100.9 %	0.31 %	3.2 %
Potassium	105	100.0 %	0.14 %	1.5 %
Magnesium	105	100.9 %	0.26 %	2.6 %
Manganese	105	101.1 %	0.22 %	2.2 %
Sodium	105	100.2 %	0.22 %	2.3 %
Silicon	105	100.0 %	0.17 %	1.8 %
Zinc	105	99.7 %	0.28 %	2.9 %

* Standard Error (%) = $100 \times \text{Mean accuracy} / \sqrt{\text{number of sample}}$

** Coefficient of Variation (CV; %) = $100 \times \text{standard deviation} / \text{mean accuracy}$

4.2.3 Analytical Precision: Matrix Duplicate Analysis

Analytical precision was evaluated by analyzing duplicate split samples prepared from the same field sample, and analytical accuracy was evaluated by analyzing matrix spike samples. Every 20th sample was prepared twice and included in each batch of field samples.

Replicate analysis precision (mean % difference of all split pairs analyzed over the year; n = 27) had an overall mean difference of 0.20% for all detected elements combined, and an overall standard error of 3.1% (Table 14). Accurate results were obtained for metal concentrations well above their detection limits: calcium (-0.23%); potassium (0.31%); magnesium (-0.84%); sodium (-1.26%). In contrast, replicate analyses of trace metal concentrations for copper, iron, zinc and manganese were near their detection limits, and thus were inherently noisy and gave high (and unrepresentative) variability. Results for those elements are not reported but are indicated by “Near Detection Limit.” Aluminum and silicon are present in most stream samples at detectable concentrations; aluminum can be near or below detection limit in some samples but easily detectable in others. Replicate precision results for aluminum (5.25%) and silicon (-

2.05%) are reasonably representative of analytical precision for those elements, relative to the concentrations found in Park stream water.

4.2.4 Analytical Accuracy: Matrix Spike Analysis

Accuracy (bias) of ICP-AES analyses was assessed by analyzing field samples spiked with known amounts of analyte and calculating percent of added-mass that was detected. Table 14 summarizes the results of all 26 spiked-samples analyzed over the year. Recovery efficiencies averaged 100.1% for all elements combined, with an overall standard error of the mean of 1.2%. Individual metals were measured with similar accuracy; mean % recovery for individual elements ranged from 98.1% to 102.4%.

Table 14. ICP-AES method precision and bias (duplicate split samples and spiked samples)

Element	Split Analysis Mean % Difference *	N	Spiked Analysis Mean % Recovery **	N
Aluminum	5.25 %	27	98.1 % (S.E. = 1.0%)	26
Calcium	-0.23 %	27	99.4 % (S.E. = 1.1%)	26
Copper	Near Detection Limit	27	100.3 % (S.E. = 0.5%)	26
Iron	Near Detection Limit	27	102.4 % (S.E. = 1.2%)	26
Potassium	0.31 %	27	101.7 % (S.E. = 0.9%)	26
Magnesium	-0.84 %	27	99.8 % (S.E. = 0.6%)	26
Manganese	Near Detection Limit	27	101.9 % (S.E. = 0.5%)	26
Sodium	-1.26 %	27	100.1 % (S.E. = 0.7%)	26
Silicon	-2.05 %	27	98.8 % (S.E. = 2.6%)	26
Zinc	Near Detection Limit	27	98.5 % (S.E. = 2.9%)	26

* Difference (%) = 100 x (absolute value of replicate results difference / replicate results mean)

** Recovery (%) = 100 x (measured analyte mass divided by the added analyte mass);
S.E. = standard error of the mean

4.3 USGS QA Reference Samples (Inter-Laboratory Comparison Study)

Certified quality assurance reference samples are obtained each year from USGS as part of a laboratory quality assessment program. The current year's USGS QA reference samples and a few USGS QA reference samples archived from prior years were analyzed at various times during the year. At least one USGS sample was included in each day's batch of samples at a rate of about one per 20 samples. Occasionally, one or more USGS samples were also included in a batch of samples as an ordinary unknown sample. Mean metal concentrations were calculated and compared to the Most Probable Values (MPV; "true" concentrations) in the certified USGS QA reference samples (found at <http://bqs.usgs.gov/srs/>). USGS QA samples analyzed this year were:

- T-217, N-121 and P-62 (Spring 2014 round),
- T-215, N-119 and P-61 (Fall 2013 round),
- T-207, N-111 and P-57 (Fall 2011)
- T-183 (Fall 2005).

Results from these USGS QA sample analyses are presented as percent deviation from the MPV reported by USGS. Samples numbers beginning with "T" identify trace element samples and were analyzed for all 10 metals. Sample numbers beginning with "N" identify samples prepared

with low concentrations of nutrients were analyzed for nitrate (as nitrogen) and ammonium (as nitrogen). Samples numbers beginning with “P” identify precipitation samples were analyzed only for base cations (sodium, potassium, magnesium and calcium), chloride, and sulfate. Due to calculation error, the values reported to USGS for samples T-215 and P-61 may differ from the corrected values reported here.

4.3.1 IC Results

Accuracy results for USGS inter-laboratory QA study samples were within the acceptable criterion of $\pm 20\%$ (Table 15). The analytical accuracy for chloride, nitrate and sulfate were $\leq 5\%$, and the accuracy for ammonium (in sample N-121) was 7%. There were two anomalous cases: nitrate and ammonium in N-119 and sulfate in P-57. The cause of the N-119 anomaly is unknown; the reproducibility of 15 replicate analyses was 1.4% (standard error) for nitrate and 1.2% for ammonium. The high precision suggests reliable laboratory technique. The fact that both analytes in the same sample deviated substantially from the known concentration suggests an issue with the stock sample. The cause of the sulfate anomaly was unknown; however, it is notable that the deviation from MPV for sulfate increases with age of sample: 2.8% for the 2014 sample; 5.1% for the 2013 sample, and 41% for the 2011 sample. The accuracy results were inconsistent with the analytical precision results for anions and ammonium in the field-collected samples (Table 15), thus, the relatively large deviations noted for ammonium and sulfate in older USGS samples could indicate deterioration of those aged samples.

Table 15. Ion chromatograph blind-sample accuracy QA summary (anions and cations)

Sample (Year)*	Constituent	Reported mg/L (# samples)	Actual (USGS)	% difference
N-121 (Spring 2014)	NH ₄ ⁺ (as N)	0.091	0.098	7.0%
	NO ₃ ⁻ (as N)	0.409 (46)	0.418	2.1 %
N-119 (Fall 2013)	NH ₄ ⁺ (as N)	0.046 (10)	0.222	-79.2%
	NO ₃ ⁻ (as N)	0.170 (15)	0.272	-37.4%
N-111 (Fall 2011)	NH ₄ ⁺ (as N)	not measured	0.280	
	NO ₃ ⁻ (as N)	0.328 (24)	0.312	5.1%
P-62 (Spring 2014)	Cl ⁻	2.40 (57)	2.37	1.4%
	SO ₄ ²⁻	1.80 (57)	1.85	2.8%
P-61 (Fall 2013)	Cl ⁻	11.96 (5)	11.9	0.5%
	SO ₄ ²⁻	0.465 (5)	0.49	5.1%
P-57 (Fall 2011)	Cl ⁻	2.26 (24)	2.24	0.8%
	SO ₄ ²⁻	0.118 (24)	0.200	-41%

* Samples consist of current and past-years' USGS Round-Robin reference quality assurance samples. UTK-CEE is designated as “lab #228” in the list of participating labs.

It is notable that the sodium and potassium are the least accurate (more than 10% of the MPV), and to a lesser extent aluminum and zinc. The reason might be related to known detection difficulties that ICP-AES instruments have for these elements. The larger bias for zinc and aluminum in the two USGS samples may be a function of concentrations being near the element's detection limit. Also notable is the change in data quality (precision and bias) for some elements over time, particularly in USGS samples T-183 (Fall 2005) and T-207 (Fall 2011), yielding more variable and less accurate data than recent USGS samples T-215 (Fall

2013) and T-217 (Spring 2014). Data for the older USGS samples were collected over this year to evaluate their relative stability. As was concluded from the assessment of IC QA data, USGS QA reference samples older than 3 years should not be used as a QA reference sample due to possible degradation of those samples.

4.3.2 ICP Results

This year's QA results for metals analyses on the ICP-AES (Table 16) had an overall mean accuracy of 104.5% (T-215), 98.7% (P-61), 105.9% (T-207) and 105.2% (T-183) for all elements combined. The analytical accuracy for individual metals was well within acceptance criterion of $\pm 20\%$; intra-element accuracy is more varied for these samples than for the QCC analytical results or for the known-addition spike recovery results. Element-specific accuracy results are within 10% of the MPV, with the following exceptions: P-61 (sodium); T-207 (potassium, sodium, zinc); T-183 (aluminum, potassium, sodium, zinc).

Table 16. ICP-AES blind-sample accuracy for USGS certified reference samples (percent)

Element	T-217 (N=10)	P-62 (N=10)	T-215 (N=4-26)	P-61 (N=11)	T-207* (N=4)	T-183* (N=7)
Aluminum	BDL	n/a	100.2% (1.9)	n/a	108.1% (1.6)	114.5% (7.1)
Calcium	103.3% (0.5)**	101.6% (0.55)	105.7% (0.9)	97.4% (1.0)	100.2% (1.9)	102.7% (1.8)
Copper	BDL	n/a	BDL	n/a	BDL	90.6% (16.7)
Iron	BDL	n/a	101.0% (2.6)	n/a	106.0% (0.7)	103.5% (1.9)
Potassium	106.6% (0.9)	102.6% (1.16)	106.8% (0.5)	108.4% (0.4)	125.4% (0.7)	116.1% (0.75)
Magnesium	102.1% (1.2)	102.1% (0.48)	101.4% (0.9)	99.6% (0.4)	103.9% (1.1)	100.6% (2.9)
Manganese	109.8% (1.0)	n/a	107.4% (1.8)	n/a	104.0% (0.5)	101.8% (1.0)
Sodium	96.8% (1.2)	94.9% (0.61)	114.2% (0.7)	89.4% (0.8)	73.6% (10.5)	83.7% (4.0)
Silicon	101.6% (0.5)	n/a	99.0% (1.7)	n/a	105.8% (0.6)	103.5% (0.7)
Zinc	94.4% (2.3)	n/a	BDL	n/a	116.1% (2.9)	135.4% (3.2)

* Use of USGS reference quality control samples T-183 (2005) and T-207 (2011) will be discontinued after this year due to suspected degradation of these samples over time.

** Standard Error (%) in parentheses = $100 \times \text{standard deviation} \div \text{square-root of number of samples}$

n/a = not applicable; BDL = below detection limit for that element

4.4 Ion Charge Balance Check

Data quality checks also include computing relative ion-charge balance for all water samples collected in the field. The ion balance is calculated by subtracting equivalent concentrations of ANC and anions from the sum of protons, cations and dissolved metals. Ideally, the difference between equivalent concentrations of anions and cations should be zero. Deviations from zero could have several causes: unmeasured dissolved ionic species, incorrect ion charge (equilibrium speciation) of dissolved metals, or poor analytical accuracy. Exhaustive analysis of samples is impractical, thus some deviation is tolerated. USEPA suggests that a charge balance deviation of $\leq 5\%$ is considered adequate recovery of measured dissolved ionic species; however, low ionic-strength samples are prone to charge balance deviations $> 10\%$ (Fritz 1994; Murray and Wade 1996). The ion balance calculations for 2013 NDW samples are summarized in Table 17.

Table 17. Ion charge balance calculations for Noland Divide Watershed samples (streamlet, precipitation, and soil water).

Ion Balance Deviation (%)	NE Streamlet	SW Streamlet	TF* (buckets)	TF* (funnels)	OS	Soil Water (upper)	Soil Water (middle)	Soil Water (lower)
Annual Mean	-7.5%	-13.0%	-13.5%	-33.0%	+4.7%	-6.5%	+14.6%	+9.7%
Sample Number (N)	17	17	7	8	12	5	16	17

* Throughfall (TF) samples collected in buckets for winter samples (November to April) and in jugs attached to funnels for summer samples (May to October).

The sign of the reported values indicate (on average) the direction of deviation; which ion charges are under-represented or over-represented. Negative deviations indicate anions are under-represented; positive deviations indicate cations are under-represented.

All except TF (funnels) are within 15% of balance. Five of the eight sample types showed negative deviations (anions under-represented). Missing (unmeasured) anions could include inorganic species such as phosphate and carbonate/bicarbonate. They could also consist of dissolved organic matter (DOM; also called dissolved organic carbon, or DOC), which typically consists of water-soluble, polar organic compounds of various molecular sizes (e.g., acetate, formate, phenate, tannate, fulvic acids and low-molecular weight humic acids). Depending on pH, these dissociate to varying degrees into negatively charged anions and cations. Since DOC analysis is not part of the current monitoring program, the amount of these materials in NDW samples is unknown; however, their presence in these samples could explain at least part of the anion-deficiency in the NDW ion balance calculations. Indirect lines of evidence for the DOC hypothesis are the magnitudes of deviation from balance:

- The anion-deficiency in summer/fall samples of TF (during high biological activity, leaf-fall and organic matter turnover) was higher than that of winter/early spring samples of TF (during low biological activity).
- The ion balance in OS samples (“pure” precipitation) were slightly positive (closest to perfect balance), indicating no missing anions. This is consistent with no DOC component in OS.
- Water samples from the upper soil horizon (which has the most influence from deposited organic matter, and the most biological activity) had a negative deviation from balance (anions under-represented), whereas water from the lower soil horizons have positive deviations from balance (indicating no missing anions).
- The ion balance in streamlet samples (NE and SW) are the same sign (direction of deviation) and order of magnitude as the winter TF and soil water from the upper soil horizon, both of which are suspected of containing a substantial concentration of DOC.

Positive deviations in soil water from the middle and lower soil horizons (indicating unaccounted cations) could indicate the presence of unmeasured dissolved minerals originating from soil and rock weathering. This is supported by relatively high total ionic strength and conductivity in those samples.

4.5 General Data Quality Assurance Improvements

Several procedures were optimized or instituted beginning this year to support the continued generation of high-quality analytical data from the UTK-CEE Water Quality Lab. These procedures are summarized in Appendix D.

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Appendix A: Algorithm for calculating monthly and annual precipitation volumes and deposition mass for NDW samples

Data Processing Procedure:

1. Open a dataset (in Excel spreadsheet format) containing precipitation sample retrieval dates, precipitation amounts per sample, and ion concentrations (nitrate, sulfate, other) in each precipitation sample.

Note: Precipitation amounts might be in any number of various units; ultimate units must be in cubic centimeters (cm³) of precipitation per square cm (cm²) of collection container opening area (cm³ / cm² = cm depth).

Note: For consistency, the day on which a precipitation samples is retrieved shall not be included in that precipitation sample's collection period. For example, a precipitation sample retrieved from the field on 15 June 2014 is assumed to represent precipitation collected since the previous sample retrieval date up through the previous day, 14 June 2014. The day on which a sample is retrieved (i.e., 15 June 2014) shall be considered part of the next sample retrieval period.

2. Sort the dataset by sample retrieval date, in order of earliest to most recent.
3. Add one row between the spreadsheet's header row and the first row of data.
4. Enter a "dummy" date to the new blank cell in the "Sample Retrieval Date" column. The date should be in the same year and month as the first data entry in the dataset, but an earlier day-of-month (e.g., first day of month).
5. Add 15 new columns to the spreadsheet. It is recommended to add the new columns to the right of the last column of the original dataset spreadsheet. The contents of the 15 columns are listed below (A through M), along with the Excel formulae that calculate the content of the columns.

Note: In the following examples, the formulae are written with the following cell-address defined:

- spreadsheet-row Row #3 contains the cells being calculated or used in calculations
- spreadsheet-column A contains the sample retrieval date,
- spreadsheet-column F contains the raw precipitation data (in centimeters)
- spreadsheet-column J contains the concentration of chemical #1 (in equivalents per liter)
- the 15 inserted columns start at spreadsheet-column AA.

- a. Year of sample retrieval date (column AA) =YEAR(\$A3)
- b. Month of sample retrieval date (column AB) =MONTH(\$A3)

- c. Define “sample collection period” as the number of days between the sample’s retrieval date and the prior sample’s retrieval date.
- d. Fraction of the “sample collection period” associated with the current month (the month of the current sample retrieval date) (column AC):

$$=IF(NOT(MONTH(\$A3)=MONTH(\$A2)),(\$A3-DATE(YEAR(\$A3),MONTH(\$A3),1))/DATEDIF(\$A2,\$A3,"d"),1)$$
- e. Fraction of the “sample collection period” associated with the prior month (the month in which the prior precipitation sample was retrieved) (column AD): $=1-AC560$
- Note: Infrequently, more than one month will have transpired between the current sample retrieval date and the prior sample retrieval date. In such cases, the “sample collection period” will be more than one month (e.g., > 31 days). The Excel formula calculations should accurately handle such cases.)
- f. Adjusted precipitation during time-interval; the precipitation amount (cm) associated with each sample retrieval date (column AE): $=(\$AC3*F3)+(\$AD4*F4)$
- g. Adjusted monthly precipitation; the total precipitation amount (cm) associated with the current month (the month of the current sample retrieval date) (column AF):

$$=IF(NOT(MONTH(\$A3)=MONTH(\$A4)),SUMIFS(AE:AE,AA:AA,YEAR(\$A3),AB:AB,MONTH(\$A3)),")$$
- h. Adjusted annual precipitation; the total precipitation amount (cm) associated with the current year (the year of the current sample retrieval date) (column AG):

$$=IF(NOT(YEAR(\$A3)=YEAR(\$A4)),SUMIF(\$AA:\$AA,YEAR(\$A3),AF:AF),")$$
- i. Deposition rate (equivalents per hectare per time-interval; eq/ha/interval) of chemical (e.g., sulfur) during time-interval associated with the current sample retrieval date (column AH): $=J3*\$F3/10$
- j. Adjusted proportional deposition rate (eq/ha/interval) of chemical (e.g., sulfur) = the proportion of the sample’s deposition rate associated with the current month (column AI):

$$=(\$AC3*AH3)+(\$AD4*AH4)$$
- k. Monthly deposition rate (eq/ha/month) of chemical (e.g., nitrate) associated with the current month (the month of the current sample retrieval date) (column AJ):

$$=IF(NOT(MONTH(\$A3)=MONTH(\$A4)),SUMIFS(AI:AI,\$AA:\$AA,YEAR(\$A3),\$AB:\$AB,MONTH(\$A3)),")$$
- l. Annual deposition mass of ion (e.g., nitrate); the deposition rate (eq/ha/year) associated with the current year (the year of the current sample retrieval date) (column AK):

$$=IF(NOT(YEAR(\$A3)=YEAR(\$A4)),SUMIF(\$AA:\$AA,YEAR(\$A3),AJ:AJ),")$$
- m. The each additional set of four columns are merely replication of columns I to L (above), applied to the next chemical of interest (e.g., nitrogen equivalents). The same Excel formulae apply, with appropriate adjustment of cell/row/column addresses.

5. Once the basic calculations in Step 4 are completed, a summary table (in a new spreadsheet page) can be created using the VLOOKUP function in Excel. That summary table will contain: the sample retrieval year (left-most column), sample retrieval month (top header row), monthly totals of precipitation (cm) and deposition rates (eq/ha/yr) or weighted-monthly concentrations (micro-Eq/L) (main body of table), and annual totals of precipitation (cm) and deposition rates (eq/ha/year) or weighted-annual concentrations (micro-Eq/L) (right-most column):

=SUMIFS(\$AG:\$AG, \$B:\$B, \$A3, \$C:\$C, B\$2)

Spreadsheet cell address definitions:

Original Data:

Excel column A:A	= "Sample Date"	sample retrieval date
Excel column F:F	= "Cum_Precip (cm)"	Precipitation amount (raw data; centimeters)
Excel column J:J	= "Lab Nitrate_IC"	Nitrate concentration (micro-Eq/L)
Excel column K:K	= "Lab Sulfate_IC"	Sulfate concentration (micro-Eq/L)

Added Columns:

Excel column B:B	= "YR"	year of sample retrieval date (formula "a")
Excel column C:C	= "MO"	month of sample retrieval date (formula "b")
Excel column D:D	= "f(currMO)"	proportion (formula "c")
Excel column E:E	= "f(lastMO)"	proportion (formula "d")

Excel column AG	= "Adj'd in-Month Precip (cm)"	Precip amount (formula "e")
Excel column AH	= "Adj'd Monthly Precip (cm)"	Precip amount (formula "f")
Excel column AI	= "Adj'd Annual Precip (cm)"	Precip amount (formula "g")

Excel column AJ	= "Sulfate Deposition per sample (Eq/ha/intvl)"	(formula "h")
Excel column AK	= "Adj'd in-Month SO4 deposition (Eq/ha/intvl)"	(formula "i")
Excel column AL	= "Adj'd Monthly SO4 deposition (Eq/ha/MO)"	(formula "j")
Excel column AM	= "Adj'd Annual SO4 deposition (Eq/ha/YR)"	(formula "k")

Excel column AN	= "T.I.N. Deposition per sample (Eq/ha/intvl)"	(formula "h")
Excel column AO	= "Adj'd in-Month T.I.N. deposition (Eq/ha/MO)"	(formula "i")
Excel column AP	= "Adj'd Monthly T.I.N. deposition (Eq/ha/MO)"	(formula "j")
Excel column AQ	= "Adj'd Annual T.I.N. deposition (Eq/ha/YR)"	(formula "k")

Etc... (additional sets of 4 columns (for formulae "h" through "k") should be added to the spreadsheet for each additional analyte or stream water component that is to be calculated).

Appendix B: Methods for Chemistry Analysis Performed at the University of Tennessee –Knoxville.

Analysis	Procedure	Equipment	Method References
pH	Potentiometric	PC-Titration Plus	EPA Method 150.1
Conductance	Potentiometric	PC-Titration Plus	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus	Automated Gran Titration for low ionic strength waters, as in Hillman et al. 1986
Anions (NO_3^- , Cl^- , SO_4^{2-})	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Monovalent Cations (NH_4^+)	Ion Chromatography	Dionex Ion Chromatograph	Manufacturers Protocols
Earth and Trace Metals (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , & Si)	Inductively Coupled Plasma Spectrometer	Thermo-Electron Iris Intrepid II	Standard Methods 3120B EPA Method 6010B EPA Method 3005A

Standard Methods, AWWA (1995).

Appendix C: Site Locations for the Park-wide Stream Water Quality Program.

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
4	Lower Rock Creek	35.7613	-83.2104	634	2	Cosby Creek	1993-
13	Little River at boundary	35.6676	-83.7145	335	5	East Little River	1993-
24	Lower West Prong Little River	35.6568	-83.7102	351	4	West Little River	1993-
30	West Prong Little Pigeon at Headquarters	35.6882	-83.5367	436	4	West Prong Little Pigeon	1993-
66	West Prong Little Pigeon at Chimneys Picnic Area	35.6372	-83.4948	817	4	West Prong Little Pigeon	1993-
71	Road Prong above barrier cascade	35.6344	-83.4703	1036	3	West Prong Little Pigeon	1993-
73	Walker Camp Prong above Road Prong	35.6348	-83.4693	1024	3	West Prong Little Pigeon	1993-
74	Walker Camp Prong above Alum Cave Creek	35.6291	-83.451	1164	2	West Prong Little Pigeon	1993-
114	Cosby Creek at log bridge	35.7486	-83.2007	765	3	Cosby Creek	1993-
137	Upper Rock Creek (Cosby Creek)	35.7462	-83.2163	838	2	Cosby Creek	1993-
138	Inadu Creek (Cosby Creek)	35.7425	-83.227	1058	2	Cosby Creek	1993-
142	Beech Creek above Lost Bottom Creek	35.6356	-83.1454	1006	3	Cataloochee	1994-
143	Lost Bottom Creek (Cataloochee Creek)	35.6363	-83.1448	1000	2	Cataloochee	1994-
144	Palmer Creek above Pretty Hollow Cr	35.639	-83.1308	911	3	Cataloochee	1993-
147	Lower Cataloochee Creek	35.6669	-83.0728	750	4	Cataloochee	1993-
148	Lower Little Cataloochee Creek	35.6691	-83.0728	754	4	Cataloochee	1993-
149	Middle Cataloochee Creek at bridge	35.6463	-83.0755	777	4	Cataloochee	1993-
173	Mill Creek above Abrams Creek	35.591	-83.8536	523	4	Abrams Creek	1993-
174	Abrams Creek below Cades Cove	35.5919	-83.8531	523	4	Abrams Creek	1993-
221	Hazel Creek above cascades	35.5463	-83.5828	1219	2	Hazel Creek	1993-
233	Walker Camp Prong above Alum Cave	35.6183	-83.4272	1297	2	West Prong Little Pigeon	1993-

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
234	Upper Road Prong	35.6098	-83.4504	1524	1	West Prong Little Pigeon	1993-
237	Walker Camp Prong at last bridge	35.6241	-83.4169	1378	2	West Prong Little Pigeon	1993-
251	Beech Flats above US 441 loop	35.6023	-83.4153	1222	2	Oconaluftee	1993-
252	Beech Flats below roadcut	35.6067	-83.4339	1426	1	Oconaluftee	1993-
253	Beech Flats above roadcut	35.6068	-83.4351	1451	1	Oconaluftee	1994-
268	Oconaluftee River below Smokemont	35.5529	-83.3094	666	5	Oconaluftee	1994-
293	Rough Fork at Caldwell House	35.6244	-83.1139	840	3	Cataloochee	1993-
310	Bone Valley Creek (Hazel Creek)	35.4999	-83.6801	683	3	Hazel	1993-
311	Hazel Creek below Haw Gap Creek	35.4938	-83.6885	657	4	Hazel	1993-
479	Hazel Creek at Campsite 86	35.4723	-83.7193	530	4	Hazel	1996-
480	Haw Gap Creek near Campsite 84	35.4947	-83.6887	666	3	Hazel	1996-
481	Little Fork above Sugar Fork Trail	35.5026	-83.7084	774	1	Hazel	1996-
482	Sugar Fork above Little Fork	35.5024	-83.7086	774	2	Hazel	1996-
483	Sugar Fork above Haw Gap Creek	35.4995	-83.6949	707	2	Hazel	1996-
484	Hazel Creek at Cold Spring Gap Trail	35.5033	-83.6593	754	4	Hazel	1996-
485	Walker Creek above Hazel Creek Trail	35.5225	-83.6310	872	2	Hazel	1996-
488	Mill Creek at Pumphouse on Forge Creek Road	35.5835	-83.8345	546	3	Abrams	1996-
489	Abrams Creek 300 m below trailhead bridge	35.5914	-83.854	521	5	Abrams	1996-
492	Camel Hump Creek off Low Gap Trail	35.7446	-83.1988	832	1	Cosby	1996-
493	Palmer Creek at Davidson Branch Trail	35.6346	-83.1194	866	4	Cataloochee	1996-

Appendix D: General Data Quality Assurance Improvements

Several procedures were optimized or instituted beginning this year to support the continuing generation of high-quality analytical data from the UTK-CEE Water Quality Lab.

USGS QA Reference Sample Age

USGS round-robin QA reference sample T-183 was obtained for the Fall 2005 USGS laboratory QA round-robin evaluation. Since that time, this sample has been stored (refrigerated) and used as one of the QA samples for ICP batch analyses. A review of measured concentrations in that sample since early 2006 indicates a possible degradation of that sample over time. The mean concentrations of analytes in that sample no longer match its MPV (Fall 2005). It is plausible that a sample stored, processed and handled for that length of time could degrade in quality.

In response to this finding, a QA policy has been instituted that QA samples (from USGS or any other independent, non-UTK source) will be used for no more than 3 years after its first use. Beginning this year, the current USGS QA reference samples will be:

- T-215 (Fall 2013), T-217 (Spring 2014) and T-219 (Fall 2014) for ICP trace metals
- P-61 (Fall 2013), P-62 (Spring 2013) and P-63 (Fall 2014) for IC electrolytes and titration parameters
- N-119 (Fall 2013), N-121 (Spring 2014) and N-123 (Fall 2014) for IC nutrients

In each year, use of samples that become older than 3 years will be discontinued, and will be replaced by the most recent USGS QA reference sample. This will provide three years of continuity for the data for any given QA reference sample, and will provide an overlap of two to three years for long-term continuity of analytical QA monitoring. Further, to provide some level of long-term continuity and comparability in reporting the analytical results for QA samples, independent of any particular QA sample, those results will be reported as a relative percentage of the sample's MPV or known concentration. Normalizing the QA results eliminates any data reporting discontinuity associated with differences in concentrations among the QA samples.

Analysis Logsheets

Documentation of analytical work is important for demonstrating data quality, tracking analytical work completed and analysis/sample details, or investigating anomalous results and developing corrective measures. Logsheets were redesigned to consolidate pertinent information previously recorded on numerous individual data sheets. On one, two-sided sheet is contained information on standards source and preparation (traceable back to batch number of primary standards), analysis run specifications (including electronic file name(s) of files generated by instrument's computer software), identification of samples run on that day's batch (including QA samples), QA sample preparation (e.g., spike sample preparation), and space for non-standard information or observations. Duplicate copies of completed logsheets are printed for day-to-day reference, as desired. Original completed logsheets are scanned into "PDF" format and securely stored electronically, and then are archived in secure, project- or analytical instrument-specific binders.

Contamination Prevention / Purity Checks

Several procedures were optimized or instituted to ensure that source water, sample preparation, or labware cleaning procedures are not contributing contamination bias to analytical results.

- **Source Water Purity Checks:** Samples of Milli-Q TM Type-1 water generated from our in-lab sources will be analyzed periodically to confirm the resistivity indicator values on the water production units.
- **Labware Rinse Water Blank Checks:** Samples of rinsings collected during labware washing operations will be analyzed periodically to confirm efficiency of wash procedures.
- **Method Blank Checks:** Periodically, samples of Milli-Q TM Type-1 water generated from in-lab sources will be processed as field samples (i.e., filtered and acidified) and analyzed to confirm the efficiency of sample processing.
- **Acid Bath Concentration Checks:** Acid-bath water will be analyzed periodically for metals to confirm the efficiency of the acid soaking process for labware.

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

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